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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME XII. DETERMINATION OF PHOSPHORUS IN GASOLINE

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Research Triangle Institute

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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME XII - DETERMINATION OF PHOSPHORUS IN GASOLINE

by

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This document presents guidelines for developing a quality assurance program for the determination of phosphorus in gasoline by the Federal reference method. These guidelines include:

1. Recommended operating practices and techniques,
2. Procedures for assessing performance and qualifying data, and
3. Procedures for identifying trouble and improving data quality.

This document is an operations manual, designed for use by laboratory personnel.

PRICES SUBJECT TO CHANGE

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Quality Assurance		13H
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Air Pollution		13B
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Phosphorus		7B

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APPENDIX D CONVERSION FACTORS

Conversion factors for converting the U.S. customary units to the International System of Units (SI)* are given below.

TO CONVERT FROM	TO	MULTIPLY BY
nanometer (nm)	micron (μ)	0.001
	Angstrom (Å)	0.1
	centimeter (cm)	10^{-7}
milligrams (mg) of phosphorus/liter	g of phosphorus/gal	0.0038
degree Celsius (°C)	degree Fahrenheit (°F)	°F = (1.8)(°C) + 32
absorbance (A)	transmittance (T)	$T = 10^{-A}$

*Metric Practice Guide (A guide to the use of SI, the International Systems of Units), American National Standard Z210.1-1971, American Society for Testing and Materials, ASTM Designation: E380-70, Philadelphia, Pa., 1971.

ABSTRACT

This document presents guidelines for developing a quality assurance program for the determination of phosphorus in gasoline by the Federal reference method. These guidelines include:

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2. Procedures for assessing performance and qualifying data, and
3. Procedures for identifying trouble and improving data quality.

This document is an operations manual, designed for use by laboratory personnel.

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SECTION I INTRODUCTION

This document presents guidelines for developing a quality assurance program for the manual (noncontinuous) determination of phosphorus in gasoline by the molybdenum blue method. This method was published by the Environmental Protection Agency in the Federal Register, July 8, 1974, and is reproduced in appendix A of this document.

This document is divided into three sections:

Section I, Introduction. The Introduction lists the overall objectives of a quality assurance program and delineates the program components necessary to accomplish the given objectives.

Section II, Operations Manual. The Operations Manual sets forth recommended equipment selection, calibration, and operating procedures to insure the collection of data of high quality and instructions for performing quality control checks designed to give an indication or warning that invalid or poor quality data are being collected, allowing for corrective action to be implemented before future determinations are made.

Section III, Quality Assurance Procedures. The Quality Assurance presents information relative to the test method, a functional analysis to identify the important operating variables and factors, and statistical properties of and procedures for conducting an independent assessment of data quality.

The objectives of this quality assurance program for the molybdenum blue method of determining phosphorus in gasoline are to:

1. Provide recommended operating procedures and techniques,
2. Identify and minimize systematic errors to maintain the precision within acceptable limits in the determination process,
3. Provide routine indications of and documentation for satisfactory performance of operating personnel and/or equipment,
4. Provide for prompt detection and correction of conditions which contribute to the collection of poor quality data, and
5. Provide the necessary information to describe the quality of the data.

To accomplish these objectives, a quality assurance program must contain the following components:

1. Recommended operating procedures,
2. Routine training of personnel and evaluation of performance of personnel and equipment,
3. Routine monitoring of the variables and parameters which may significantly affect data quality, and
4. Development of statements and evidence to qualify data and detect defects.

Implementation of a quality assurance program will result in data that are more uniform in terms of precision and accuracy. It will enable each monitoring network to continuously generate data that are of acceptable quality.

The scope of this document has been purposely limited to that of a laboratory manual.

SECTION II OPERATIONS MANUAL

2.0 GENERAL

This operations manual sets forth recommended operating procedures for the spectrophotometric determination of phosphorus in gasoline by using the molybdenum blue method (ref. 1). This method is reproduced from the Federal Register in appendix A of this document. Quality control procedures and checks designed to give an indication or warning that invalid or poor quality data are being collected are written as part of the operating procedures and are to be performed by the operator on a routine basis.

In this method the gasoline sample is adsorbed on zinc oxide and ignited. The phosphorus is determined in the presence of the zinc using the molybdenum blue method, which was studied extensively by Mellon and Kitson (ref. 2). The color obtained is stable and reproducible in the presence of zinc and lead ions, tetraethyllead, scavengers, antioxidants, metal deactivators, sulfur, or manganese antiknock compounds (ref.3).

The color development results from the condensation of orthophosphoric and molybdic acids to heteropoly complex compounds, the molybdophosphoric acids (refs. 4,5). The reduction of these molybdophosphoric acids produces a blue color; the color intensity is proportional to the amount of orthophosphate ions incorporated in the complex. The exact constitution of these reduction products is uncertain, but their formation is reproducible (ref. 6). Complex formation is carried out in an acidic solution at pH less than 1. The color intensity is stronger in a less acidic solution, but the color developed by the reagents is also much greater. The color intensity does not increase in the presence of excess reducing agent, hydrazine sulfate.

In measuring the intensity of a heteropoly blue solution, the color, once developed, cannot be diluted or concentrated because the intensity depends on the pH, the molybdenum-acid ratio, and the amount of molybdate (refs. 7,8). With a given concentration of molybdate, a minimum concentration of acid is required to prevent color development in the absence of phosphate. Just above this critical concentration there is a limited range in which the intensity of the color is proportional to the phosphate content almost independently of the acidity. Further increases in acidity cause a decrease in color intensity (ref. 5).

The accuracy of data obtained from this method depends upon equipment calibration and the proficiency with which the operator performs his various tasks. This determination method from reagent preparation through sample analysis and data reporting is a complex operation. Guidelines are presented with special emphasis on quality control checks and decision rules applicable to known problem areas. The operator should make himself familiar with the rules and regulations concerning the reference method as written in the Federal Register, Vol. 39, No. 131, Part 80, July 8, 1974 (reproduced as appendix A of this document for convenience of reference).

Instructions throughout this document are directed primarily toward an 8-hour determination period--i.e., an 8-hour workday in which it is assumed that approximately 8 P determinations can be made. Also, an auditing or checking level of a minimum of once a week or every time a field sample exceeds the Federal standard is recommended (see subsection 3.3.2). Sampling period durations and auditing levels are subject to change by the supervisor and/or manager. Such changes would not alter the basic directions for performing the operation. Also, certain quality control limits as given in this manual represent best estimates for use in the beginning of a quality assurance program and are, therefore, subject to change as field data are collected.

It is assumed that all apparatus satisfies the reference method specifications and that the manufacturer's recommendations will be followed when using a particular instrument (e.g., spectrophotometer).

The sequence of operations to be performed during each determination period is given in figure 1. Certain operations such as preparation of certain reagents and spectrophotometer calibration are performed periodically. The remaining operations are performed during each determination period. The operations are classified as equipment selection, calibration, sample analysis, and data processing. Each operation or step in the process is identified by a block. Quality checkpoints in the determination process, for which appropriate quality control limits are assigned, are represented by blocks enclosed by heavy lines. Other checkpoints involve go/no-go checks and/or subjective judgments by the analyst with proper guidelines for decisionmaking spelled out in the procedures. These operations and checks are discussed sequentially as one progresses step by step through the sequence of actions in figure 1.

The analyst is responsible for maintaining certain records. Specifically, the following log books are maintained:

EQUIPMENT SELECTION

1. Select the equipment according to specifications given in the reference method (section 4, appendix A) and according to subsection 2.1.

2. Perform visual and operational checks of equipment according to subsection 2.1.1.

3. Record new equipment in a receiving record file according to subsection 2.1.1.

CALIBRATION

4. Calibrate the equipment according to subsection 2.2.

SAMPLE ANALYSIS

5. Identify the sample and document it according to subsection 3.2.1.

6. Prepare reagents according to subsection 2.2.

7. Analyze samples according to subsection 2.3.3.

DATA PROCESSING

8. Perform calculations to determine phosphorus content according to subsection 2.4.

9. Validate data by comparing determined value of reference sample to the known value according to subsection 2.6.

10. Report data according to subsection 2.5.

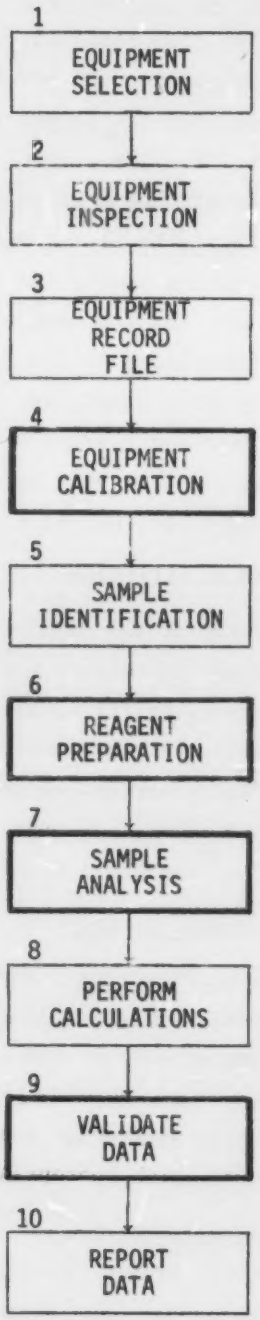

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Figure 1. [illegible] flow chart of the [illegible]

1. Receiving Record Log Book. This book contains a description of the item received, its serial number or catalog number when appropriate, and results of the acceptance test, signed and dated.
2. Calibration Record Log Book. This book contains the phosphorus calibration curves, standard sample data, and the calibration of all the equipment.
3. Sample Receiving Record Log Book. This book contains the test station sample and laboratory identifications data for each test station sample received.
4. Laboratory Test Record Log Book. This book contains the test station sample and laboratory identifications, calculation data and test information.

The Sample Receiving Record Log Book can, if desired, be combined with the Laboratory Test Record Log Book.

2.1 EQUIPMENT SELECTION

A listing of the required equipment with certain pertinent specifications is given in table 1 and in section 4 of appendix A. Additional specifications, criteria, or design features are given herein to aid in the procurement of equipment to insure the collection of data of acceptable quality. Also, procedures and limits for acceptance checks of new equipment are presented. In addition, a descriptive title and the identification number of new equipment should be recorded in the receiving record log book.

2.1.1 Spectrophotometer

2.1.1.1 Specifications. The spectrophotometer should be an instrument equipped with a tungsten lamp, a near-infrared-sensitive phototube capable of operation at 820 nm with a maximum spectral bandwidth of 10 nm and with a cell compartment capable of holding cells with a 5-cm pathlength. The radiation beam should be perpendicular to the cell window when placed in the cell holder.

2.1.1.2 Acceptance Check. The instrument should be checked out according to the manufacturer's instructions and the wavelength calibrated according to the instructions set forth in subsection 2.2.

2.1.1.3 Documentation. Record in the receiving record log book a description of the spectrophotometer, its serial number, and the results of the acceptance check, except the wavelength calibration which is recorded in the calibration record log book. Sign and date the entry.

Table 1. List of Equipment.

Apparatus	Quantity
Spectrophotometer, instrument equipped with a tungsten lamp and a near-infrared-sensitive phototube capable of operating at 820 nm with a maximum spectral bandwidth of 10 nm and with absorption cells that have 5 cm pathlengths.	1
Absorption cells, equipped with windows that are transparent to infrared radiation at 820 nm and possessing a light pathlength of 5 cm.	2
Constant-temperature bath, capable of maintaining the temperature at 82 to 88 °C and equipped to hold ten 100 mℓ volumetric flasks submerged to the mark.	1
Cooling bath, equipped to hold ten 100 mℓ volumetric flasks submerged to the mark in the ice water.	1
Oven, capable of maintaining a temperature at 105 to 110 °C for 3 hours.	1
Muffle Furnace, capable of heating camples to 704 °C.	1
Filter paper, Type II, Class G, as designated in ASTM Standard Specification D1100, 12.5 cm diameter.	1 box
Filtering Funnel, bowl with 60° angle, depressed flutings, and 75 mm diameter.	1
Ignition disk, porcelain evaporating dish, glazed inside and outside, with pour-out size number 00A, inside diameter of 75 mm and capacity of 70 mℓ.	1
Thermometer with range 10 to 105 °C.	1
Volumetric flask, 0.100 ℓ volume with ground glass stopper.	10
Volumetric flask, 1.000 ℓ volume with ground glass stopper.	2

Table 1 (continued).

Apparatus	Quantity
Syringe, 10 mℓ volume equipped with a 5 cm, 22 gauge needle.	1
Buret, 10 mℓ volume with 0.05 mℓ subdivisions.	1
Graduated cylinder, 1.000 ℓ volume.	1
Graduated cylinder, 225 mℓ volume.	1
Glass flask, 1.000 ℓ volume.	1
Pipet, 10 mℓ volume.	1
Pipet, 25 mℓ volume.	1
Glass beaker, 1.5 ℓ volume.	1
Reagents	
Sulfuric acid, reagent grade.	225 mℓ
Distilled water.	3.2 ℓ
Ammonium molybdate tetrahydrate.	20 g
Ethylene glycol, technical grade (or other suitable high-boiling bath liquid with a boiling point greater than about 100 °C).	4 gal
Hydrazine sulfate.	1.5 g
Potassium dihydrogen phosphate.	5 g
Zinc oxide, with density of approximately 0.5 g/cm^3	
Bunsen burner.	1
Propane gas.	Several liters
Face shield.	1
Rubber gloves.	1
Rubber apron.	1

2.1.2 Constant-Temperature Bath

2.1.2.1 Specifications. The constant-temperature bath should be equipped to hold ten 100 mℓ volumetric flasks submerged to the mark. The bath must have a large enough heat reservoir or water capacity, about 4 gallons, to keep the temperature between 82° and 87°C during the entire period of sample heating, which will be about 25 minutes. A good bath should maintain the temperature within ±2°C.

2.1.2.2 Acceptance Check. The bath should be checked out according to the manufacturer's instructions and calibrated according to instructions set forth in subsection 2.2.

2.1.2.3 Documentation. Record in the receiving record log book a description of the bath, its serial number and the results of the acceptance check, except the calibration results which should be recorded in the calibration record log book. Sign and date the entry.

2.1.2 Absorption Cells

2.1.3.1 Specifications. The absorption cell should be matched properly, possess windows which are parallel and transparent in the near-infrared regions, and exhibit a radiation pathlength of 5 cm.

2.1.3.2 Acceptance Check. The cells should be inspected for scratches, and their pathlengths and parallelisms insured by the manufacturer.
Note 1: As long as the use of an absorption cell is dedicated to either a reference or sample, the pathlength and parallelism will be invariant, thus precluding measurements of their values.

2.1.3.3 Documentation. Record in the receiving record log book a description of the cells, the numbers inscribed on the cells (performed by operator, if necessary), and the results of the acceptance check. Sign and date the entry.

2.1.4 Glassware

2.1.4.1 Specifications. All glassware shall be class A, volumetric glassware (ref. 9).

2.1.4.2 Acceptance Check. The volumetric glassware is inspected for cracks, scratches, and damage before it is calibrated according to the instructions set forth in subsection 2.2.

2.1.5 Oven

2.1.5.1 Specifications. The oven should be capable of maintaining a temperature of 105 to 110°C for 3 hours.

2.1.5.2 Acceptance Check. The proper operation and temperature stability of the oven should be demonstrated according to manufacturer's instructions.

2.1.5.2 Documentation. Record in the receiving record log book a description of the oven, its serial number, and the results of the acceptance check. Sign and date the entry.

2.1.6 Reagents

2.1.6.1 Specifications. Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available (ref. 4). Other grades may be used, provided it is first ascertained through measurement of samples of known concentrations that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

2.1.6.2 Acceptance Check. Ascertain that the chemicals are reagent grade and conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.

2.1.6.3 Documentation. Record in the receiving record log book a description of the reagent, its lot number, manufacturer, and results of the acceptance check. Sign and date the entry.

2.1.7 Distilled Water

2.1.7.1 Specifications. Distilled water shall be understood to mean water free from organic and phosphate materials. It should preferably be double-distilled from all-glass apparatus.

2.1.7.2 Acceptance Check. The purity of the water should be ascertained when the water is purchased or prepared and before preparing reagent solutions for analysis, according to the instructions published in subsection 2.2.

2.1.7.3 Documentation. Record in the receiving record log book the source of the water and the results of the acceptance check. Sign and date the entry.

2.1.8 Syringes

2.1.8.1 Specifications. Syringes should be 10 mℓ volume with 5 cm, 22 gauge needles.

2.1.8.2 Acceptance Check. The syringes should be inspected for scratches and cracks before calibration according to the instructions for glassware in subsection 2.2

2.1.8.3 Documentation. Record in the receiving record log book the description of the syringe, its manufacturer and catalog numbers, and the results of the acceptance check, except the calibration data which should be recorded in the calibration record log book. Sign and date the entry.

2.2 CALIBRATION

2.2.1 Glassware Cleaning

All glassware for this method must be dedicated to this experiment. No commercial detergents must be used in cleaning the glassware because these compounds often contain alkali phosphates which are strongly adsorbed by the glass surfaces during an 8-hour soak and are not removed by ordinary rinsing.

An initial wash for all glassware should consist of an 8-hour soak in 1+1 (Vol to Vol) solution of sulfuric acid and water, maintained at about 82°C, and followed by several rinses with distilled water.

2.2.2 Glassware Calibration

The accuracy of certain glassware is critical to determining the true quantity of phosphorus in gasoline. This glassware would include the apparatus used for delivering a known quantity of gasoline to the zinc oxide and for preparing standard solutions. Class A volumetric glassware purchased from reliable manufacturers is generally sufficiently accurate. It is suggested that glassware need not be calibrated unless its capacity is in doubt as a result of not being able to measure the concentration of a reference sample (a gasoline sample of known concentration) within 0.05 mg P/ℓ of its known value.

The calibration of the volumes of this glassware, when necessary, should be performed according to the following procedure or other acceptable

methods (ref. 4). The glassware to be calibrated must be scrupulously cleaned as described previously. The distilled water and glassware should be allowed to stand for a couple of hours in the room in which the calibration is to be made before operations are begun, in order that the glassware may assume the temperature of the air. The room temperature should be as constant as possible to preclude the possibility of volume changes during the calibration. Ordinary distilled water is used; it need not be air free. A thermometer graduated in single degrees is suitable for obtaining the temperature of the water. Temperatures should be read to the nearest 0.5°C.

The glassware is calibrated by weighing the amount of distilled water contained or, if applicable, delivered at the standard temperature of 20°C and calculating the volume from the density of water at 20°C, 0.9982 g/cm^3.

2.2.2.1 Documentation. Record the description of the calibrated glassware and its calibration, if required, in the calibration record log book. Sign and date the entry.

2.2.3 Distilled Water

2.2.3.1 Test for Phosphate. To 2-3 drops of the distilled water add 1-2 drops of nitric acid; add 10 drops of ammonium molybdate solution as discussed in subsection 2.2.4.1; warm to 60°-80°C (keep below boiling); and look for the formation of a bright yellow precipitate $(NH_4)_3\text{-}P(Mo_3O_{10})_4$. If a yellow precipitate forms, the remaining water should be redistilled.

2.2.3.2 Test for Purity. Distilled water can be tested for purity from oxidants in the following manner:

1. Add 0.20 mℓ of $KMnO_4$ solution (0.316 g/ℓ) to a mixture of 500 mℓ of the distilled water and 1 mℓ of H_2SO_4 in a stoppered bottle of chemically resistant glass.
2. If the permanganate color (blue) does not disappear completely after standing 1 hour at room temperature, consider the water suitable for use.

3. If the permanganate does disappear, the water must be purified before using.

2.2.3.3 Purification Procedure. Water failing the purity test can be purified as follows:

1. Add one crystal each of potassium permanganate and barium hydroxide for each liter of distilled water.
2. Redistill the water in an all-glass still.
3. Perform the test for purity as described above.
4. Repeat the purification procedure and the test for purity until the water checks pure.

This distilled water, free of oxidants, is used whenever water is required in preparing reagents for sampling or analysis.

2.2.3.4 Storage of Distilled Water. Oxidant-free water should at all times be protected from atmospheric contamination by storing in containers made of material that has been proven to be resistant to solvation by or reaction with water. Also, any tubing used during reagent preparation should be of high resistant material. Also, when removing water from the storage container, the replacement air should be drawn through a vent guard (e.g., a drying tube filled with equal parts of 8-20-mesh soda lime, oxalic acid, and 4-8-mesh calcium chloride, each compound being separated from the other by a glass wool plug).

2.2.3.5 Documentation. Record in the calibration record log book the source of the distilled water and the tests for phosphate and purity. Sign and date the entry.

2.2.4 Reagent Preparation

The analytical balance should be checked before preparing a batch of reagents by weighing a standard weight between 1 and 3 grams. If the measured and actual weights agree within ±0.2 mg, proceed with the preparation. Record the actual and measured weights in the calibration record log book. If the weights differ by more than ±0.2 mg, report to the supervisor that the balance calibration needs checking before continuing. The balance should be repaired and/or calibrated by a qualified repairman.

2.2.4.1 Ammonium Molybdate Solution. Wearing a face shield, rubber gloves, and a rubber apron, add slowly, with continuous stirring, 225 mℓ of concentrated sulfuric acid (assay as H_2SO_4 at 95 to 98 percent) to 500 mℓ of distilled water contained in a liter beaker placed in the cooling bath. Cool the solution to room temperature and add 20 g of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\text{-}4H_2O$). Stir the solution until the tetrahydrate is completely dissolved and transfer the solution to a 1.000 ℓ volumetric flask. Dilute to the mark with distilled water and store in the volumetric flask stoppered with glass.

2.2.4.2 Hydrazine Sulfate Solution. Dissolve 1.5 g of hydrazine sulfate ($H_2NNH_2 \cdot H_2SO_4$) in 1.000 ℓ of distilled water, measured with a graduated cylinder. This solution is unstable. Store it in a tightly glass-stoppered amber-colored or opaque glass container and in the dark. Prepare a fresh solution after 3 weeks or at any sign of the solution's turning light brown.

2.2.4.3 Molybdate Hydrazine Reagent. Pipet 25 mℓ of ammonium molybdate solution into a 100 mℓ volumetric flask containing approximately 50 mℓ of water, add by pipet 10 mℓ of $N_2NNH_2 \cdot H_2SO_4$ solution and dilute to 100 mℓ with water. This reagent is unstable but has been reported as stable up to 4 hours. It is our recommendation that the reagent be prepared immediately before use in analysis. The flask should be stoppered with a glass plug except when transferring to the sample. Each determination (including the blank) uses 50 mℓ.

2.2.4.4 Phosphorus, Stock Standard Solution (1.000 mg P/mℓ). Dry approximately 5 g of potassium dihydrogen phosphate (KH_2PO_4) in an oven at 105° to 110°C for 3 hours. Dissolve 4.393 ± 0.002 g of the dihydrogen phosphate reagent in 150 mℓ, measured with a graduated cylinder, of H_2SO_4 (1 volume acid to 10 of water) contained in a 1.000 ℓ volumetric flask. Dilute with water to the mark and store in the volumetric flask plugged with a glass stopper.

2.2.4.5 Phosphorus, Standard Solution (10.00 µg P/mℓ). Prepare by pipetting 10 mℓ of stock standard phosphorus solution into a 1.000 ℓ volumetric flask and dilute to the mark with distilled water. Keep the flask plugged with a glass stopper. It is unnecessary to prepare

the standard phosphorus solution daily because it keeps well. Prepare the solution weekly.

2.2.4.6 Sulfuric Acid (1+10, volume of acid to water). Wearing a face shield, rubber gloves, and a rubber apron, add slowly, with continuous stirring, 100 mℓ of concentrated sulfuric acid (H_2SO_4, sp gr 1.84), measured with a graduated cylinder, to a liter of distilled water contained in a 1.5 ℓ beaker placed in the cooling bath.

2.2.4.7 Documentation. Record in the calibration record log book the dates of the preparations of the reagent solutions, the source and lot numbers of the reagent chemicals. Sign and date the entry.

2.2.5 Constant-Temperature Bath

The constant-temperature bath shall be calibrated by operating the bath filled with ethylene glycol at 85°C for 25 minutes, during which time the temperature should be recorded every 5 minutes. The bath should maintain this temperature to within ±2°C.

2.2.5.1 Documentation. Record in the calibration record log book a description of the constant-temperature bath and the results of the calibration.

2.2.6 Spectrophotometer

2.2.6.1 Wavelength Calibration. Convenient wavelength calibration points for the near-infrared, 600 to 2500 nm, are furnished by 10 cm lengths of gaseous ammonia which has bands at these wavelengths: 1513, 1967, and 2264 nm (ref. 10).

2.2.6.2 Absorbance Calibration. The calibration curve of µg of phosphorus versus absorbance is quite reproducible. Once this curve is obtained, it should only be necessary to check its calibration each time that it is used by measuring the absorbance of the standard sample and comparing the measured value of phosphorus with its known value. The phosphorus calibration curve must be recalibrated when new stock reagent solutions are prepared, when the spectrophotometer receives major maintenance, and/or when the standard sample fails the performance check.

The absorbance of the spectrophotometer shall be calibrated as follows:

1. Transfer by buret, or a volumetric transfer pipet, 0.0,

0.50, 1.00, 1.50 and 2.00 ml of phosphorus standard solution into 100 ml volumetric flasks.

2. Pipet 10 ml of H_2SO_4 (1 + 10 by volume) into each flask. Mix immediately by swirling.
3. Prepare the molybdate-hydrazine solution. Prepare sufficient volume of reagent based on the number of samples being analyzed.
4. Pipet 50 ml of the molybdate-hydrazine solution to each volumetric flask. Mix immediately by swirling.
5. Dilute to 100 ml with distilled water.
6. Mix well and place in the constant-temperature bath so that the contents of the flask are submerged below the level of the bath. Maintain bath temperature at 82° to 88°C for 25 minutes.

Note 2: If the temperature of the constant-temperature bath drops below 82°C, the color development may not be complete. The flasks can either be clamped in the bath, or a lead ring can be placed on the neck of the flask to prevent their turning over in the bath. The liquid of the sample should be completely submerged.

7. Transfer the flask to the cooling bath and cool the contents rapidly to room temperature. Do not allow the samples to cool more than 2.8°C below room temperature.

Note 3: Place a chemically clean thermometer in one of the flasks to check the temperature. Remove the samples from the bath when their temperature is 5° above room temperature. If the samples are chilled, they will fog the windows of the spectrophotometer, and if the samples, once removed, are allowed to stand, restopper the flasks to prevent oxidation in air.

8. After cooling the flasks to room temperature, remove them from the cooling water bath and allow them to stand for 10 minutes at room temperature.
9. Using the 2.0 ml phosphorus standard in a 5 cm cell, determine the wavelength near 820 nm that gives maximum absorbance. The wavelength giving maximum absorbance should not exceed 830 nm.

10. Using a red-sensitive phototube and 5 cm cells, adjust the spectrophotometer to zero absorbance at the wavelength of maximum absorbance using distilled water in both cells. Use the wavelength of maximum absorbance in the determination of calibration readings and future sample readings.

Note 4: The sample and reference cells must be dedicated solely to this function and must be reproducibly positioned in the cell holder to attain satisfactory precision. It is essential that all measurements be made at the same value of the exit slit width.

11. The use of 1 cm cells for the higher concentrations is permissible.

12. Measure the absorbance of each calibration sample including the blank (0.0 ml phosphorus standard) at the wavelength of maximum absorbance with distilled water in the reference cell.

Note 5: Great care must be taken to avoid possible contamination. If the absorbance of the blank exceeds 0.04 (for 5 cm cell), check for source of contamination. It is suggested that the results be disregarded and the test be rerun with fresh reagents and clean glassware.

13. Correct the absorbance of each standard solution by subtracting the absorbance of the blank (0.0 ml phosphorus standard).

14. Prepare a calibration curve, as shown in figure 2, by plotting the corrected absorbance of each standard solution against micrograms of phosphorus. One milliliter of phosphorus standard solution provides 10 µg of phosphorus.

15. Use regression analysis to obtain a best-fit line to the data points. Check the plotted points; any that deviate more than 0.4 µg P should be rerun and the average of the two used.

16. Forward the calibration curve and related data to the supervisor for his approval.

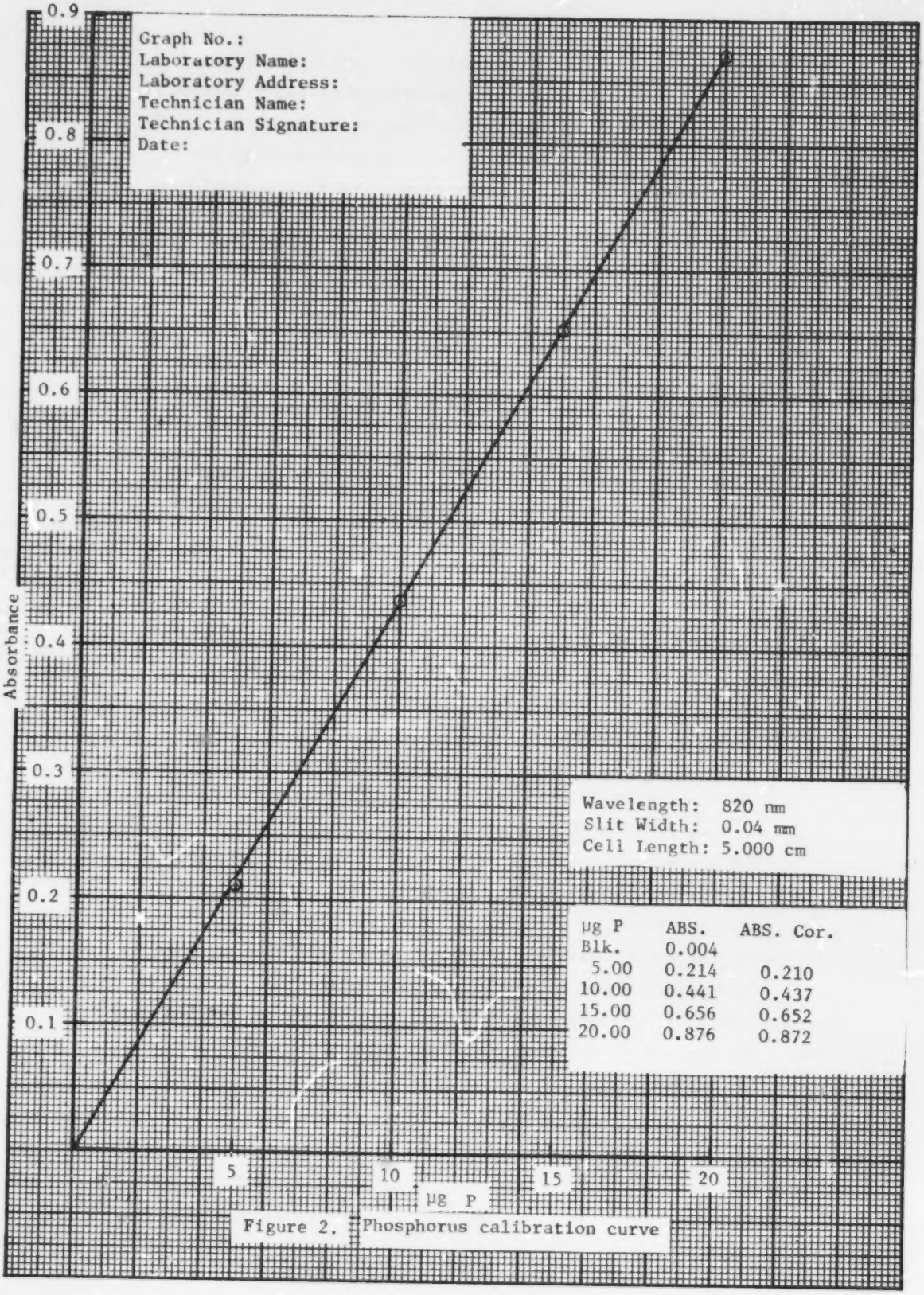


Figure 2. Phosphorus calibration curve

2.2.6.3 Documentation. Record in the calibration record log book the spectrophotometer wavelength and absorbance calibrations.

2.3 ANALYSIS

2.3.1 Sample Receiving Procedure

Samples as received from the field must be labeled with at least the following information:

1. Time of station test,
2. Date of station test,
3. Location of station,
4. Sample number,
5. Inspector's name and title,
6. Inspector's signature.

These data should be recorded in a sample receiving log book as shown in figure 3. At this time, each sample should be assigned a laboratory analysis number. This number should be placed in the sample receiving log book and on the chain-of-custody label.

2.3.2 Sample Handling Procedure

The sample should be handled and stored in accordance with safety procedures for flammable liquids. Since light fractions of a gasoline sample evaporate easily, it is recommended that the samples be stored in an explosion-proof refrigerator. Before analysis, the sample should attain room temperature. The sample must be tightly covered at all times except when removing aliquots for analysis.

2.3.3 Sample Analysis Procedure

The sample analysis procedure is illustrated in figure 4* and is listed in the following steps:

1. Selection of the size of the sample to be tested depends on the expected concentration of phosphorus in the sample. If a concentration of phosphorus is suspected to be less than 1.0 mg/ℓ, it will be necessary to use 10 mℓ of sample.

Note 6: Two grams of zinc oxide cannot absorb this volume of gasoline. Therefore, the 10 mℓ sample is ignited in aliquots

*A looseleaf, oversized flow chart for wall mounting is supplied in the rear of the report.

SAMPLE RECEIVING RECORD

1. Test Station Sample Identification

   Test Station Sample Number:

   Test Station Location:

   Region:

   Date of Station Test: / /
   MO DA YR

   Time of Station Test: :
   HR MIN

   Inspector's Name:

   Inspector's Title:

2. Laboratory Identification

   Laboratory Name:

   Laboratory Address:

   Laboratory Analysis Number:

3. Laboratory Technician

   Name:

   Signature:

   Date:

Figure 3. Sample receiving record

Reproduced from best available copy.

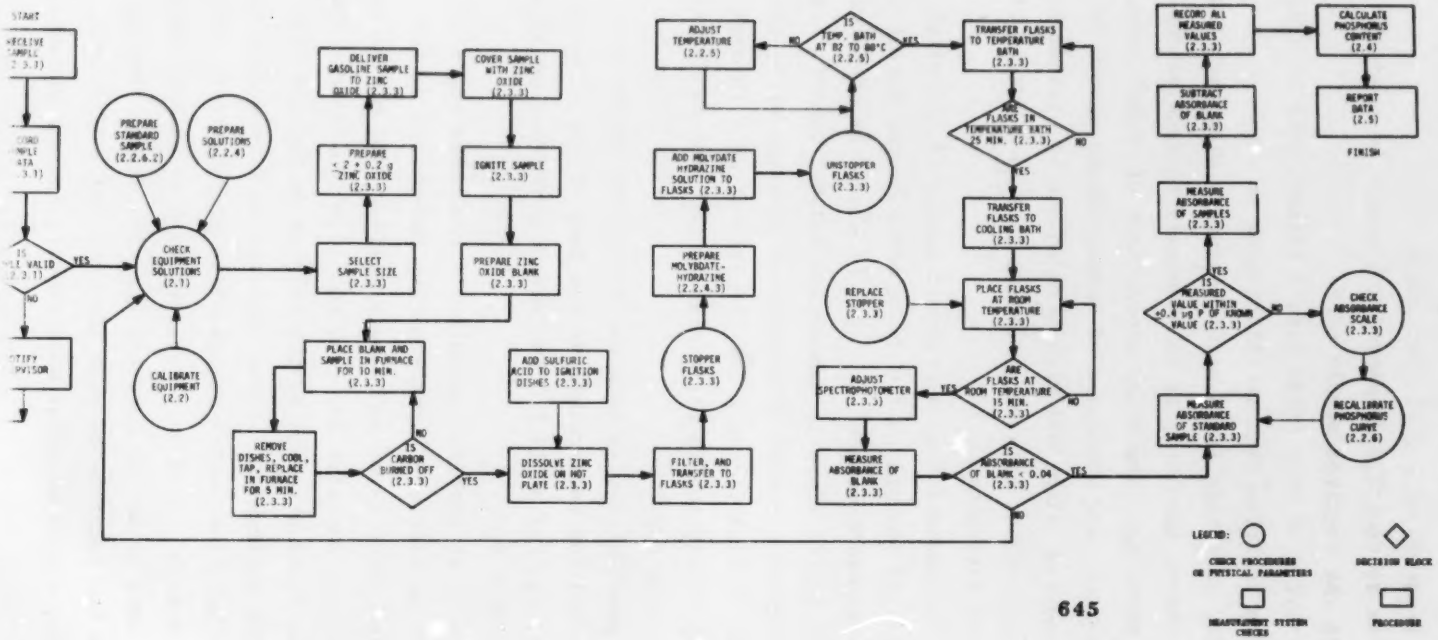

START
PREPARE STANDARD SAMPLE (2.2.6.2)
PREPARE SOLUTIONS (2.2.4)
CHECK EQUIPMENT SOLUTIONS (2.1)
CALIBRATE EQUIPMENT (2.2)
YES
NO
DELIVER GASOLINE SAMPLE TO ZINC OXIDE (2.3.2)
COVER SAMPLE WITH ZINC OXIDE (2.3.3)
PREPARE < 2 + 0.2 g ZINC OXIDE (2.3.3)
IGNITE SAMPLE (2.3.3)
SELECT SAMPLE SIZE (2.3.3)
PREPARE ZINC OXIDE BLANK (2.3.3)
PLACE BLANK AND SAMPLE IN FURNACE FOR 10 MIN. (2.3.3)
ADD SULFURIC ACID TO IGNITION DISHES (2.3.3)
REMOVE DISHES, COOL, TAP, REPLACE IN FURNACE FOR 5 MIN. (2.3.3)
IS CARBON BURNED OFF (2.3.3)
DISSOLVE ZINC OXIDE OR HOT PLATE (2.3.3)
FILTER, AND TRANSFER TO FLASKS (2.3.3)
STOPPER FLASKS (2.3.3)
PREPARE MOLYBDATE-HYDRAZINE (2.2.4.3)
ADD MOLYDATE HYDRAZINE SOLUTION TO FLASKS (2.3.3)
ADJUST TEMPERATURE (2.2.5)
IS TEMP. BATH AT 82 TO 88°C (2.2.5)
UNSTOPPER FLASKS (2.3.3)
TRANSFER FLASKS TO TEMPERATURE BATH (2.3.3)
ARE FLASKS IN TEMPERATURE BATH 25 MIN. (2.3.3)
TRANSFER FLASKS TO COOLING BATH (2.3.3)
PLACE FLASKS AT ROOM TEMPERATURE (2.3.3)
REPLACE STOPPER (2.3.3)
ARE FLASKS AT ROOM TEMPERATURE 15 MIN. (2.3.3)
ADJUST SPECTROPHOTOMETER (2.3.3)
MEASURE ABSORBANCE OF BLANK (2.3.3)
IS ABSORBANCE OF BLANK < 0.04 (2.3.3)
RECORD ALL MEASURED VALUES (2.3.3)
SUBTRACT ABSORBANCE OF BLANK (2.3.3)
MEASURE ABSORBANCE OF SAMPLES (2.3.3)
IS MEASURED VALUE WITHIN ±0.4 µg P OF KNOWN VALUE (2.3.1)
MEASURE ABSORBANCE OF STANDARD SAMPLE (2.3.3)
CHECK ABSORBANCE SCALE (2.3.3)
RECALIBRATE PHOSPHORUS CURVE (2.2.6)
CALCULATE PHOSPHORUS CONTENT (2.4)
REPORT DATA (2.5)
FINISH
LEGEND:
CHECK PROCEDURES OR PHYSICAL PARAMETERS
DECISION BLOCK
MEASUREMENT SYSTEM CHECKS
PROCESSES

Figure 4. Flow chart for the analysis of phosphorus in gasoline.

of 2 mℓ in the presence of 2 g of zinc oxide.

2. The table in section 7.2 of appendix A should be used in determining the required sample size.

3. Transfer 2±0.2 g of zinc oxide into a conical pile in a clean, dry unetched ignition dish as illustrated in figure 5.

Note 7: In order to obtain satisfactory accuracy with the small amounts of phosphorus involved, it is necessary to take extensive precautions in handling. The usual precautions of cleanliness, careful manipulation, and avoidance of contamination should be scrupulously observed also, all glassware should be cleaned before use with cleaning acid or by some procedure that does not involve use of commercial detergents.

Note 8: It is recommended that a standard sample of the stock standard solution of phosphorus (10.00 µg P/mℓ) be run during the analysis. This standard sample (1.3 mg P/ℓ) should be prepared according to the instructions in subsection 2.2.6.2 wherein 1.30 mℓ of the stock standard solution of phosphorus is transferred into a 100 mℓ volumetric flask in step 1. Complete steps 2 through 13.

4. Make a deep depression in the center of the zinc oxide pile with a stirring rod.

5. Pipet the gasoline sample into the depression in the zinc oxide. Record the temperature of the fuel if the phosphorus content is required at 15.6°C and make corrections as directed in subsection 2.4.

Note 9: For the 10 mℓ sample, use multiple additions and a syringe. Hold the tip of the needle at approximately two-thirds of the depth of the zinc oxide layer and slowly deliver 2 mℓ of the sample; fast sample delivery may give low results. Give sufficient time for the gasoline to be absorbed by the zinc oxide because fast delivery from the syringe will cause evaporation from expansion. When adding the gasoline, watch the gasoline migrate to the edge of the ZnO and then stop. In some cases, even a 2 mℓ aliquot cannot be added. The idea is not to saturate the zinc oxide. Before ignition, allow the gasoline to soak into the ZnO. After the initial ignition, carbon material will result, and the amount of

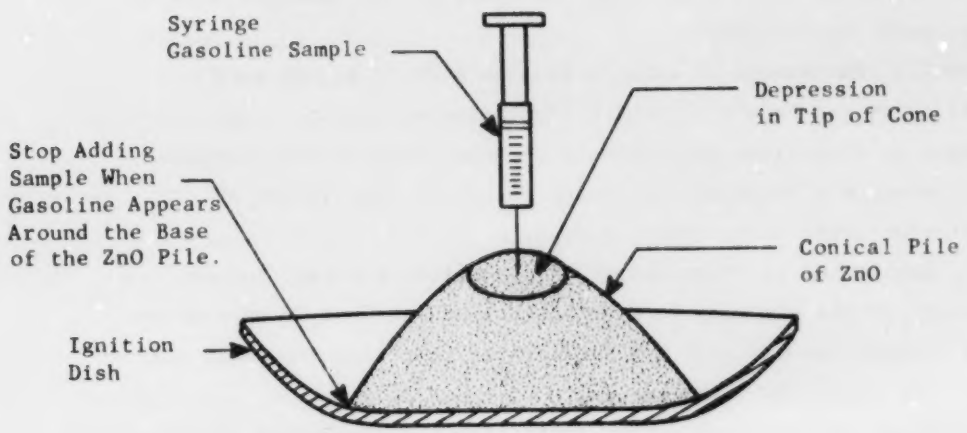


Figure 5. Illustration of the addition of sample to the zinc oxide.

gasoline that the ZnO will hold is less. Safety: After flashing the sample, allow the crucible and contents to cool to room temperature (check temperature of crucible to the touch) before making another addition of gasoline.

6. Cover the sample with a samll amount of fresh zinc oxide from the reagent bottle (use the tip of a small spatula to deliver approximately 0.2 g). Tap the sides of the ignition dish to pack the zinc oxide.

Note 10: The amount of zinc oxide should be ≤2 g; too much zinc oxide can result in a high blank (see next step). The amount of zinc oxide waste should be consistent between samples.

7. Prepare a blank of zinc oxide using the same amount of zinc oxide in an ignition dish.

8. Ignite the gasoline using the flame from a bunsen burner. Allow the gasoline to burn to extinction. For 10 mℓ samples, repeat the addition and ignition of 2 mℓ aliquots until all the sample has been burned.

9. Place the ignition dishes containing the sample and blank in a hot muffle furnace set at a temperature of 621° to 704°C for 10 minutes. Remove and cool the ignition dishes. When cool, gently tap the sides of the dish to loosen the zinc oxide. Again place the dishes in the muffle furnace for 5 minutes. Remove and cool the ignition dishes to room temperature. The above treatment is usually sufficient to burn the carbon. If the carbon is not completely burned off, place the dish in the oven for additional 5-minute periods until it is completely burned off.

Note 11: The decomposition of organic matter may also be accomplished by heating the ignition dish with a Meker burner, gradually increasing the intensity of heat until the carbon from the sides of the dish has been burned and then cooling to room temperature. However, the muffle furnace is recommended.

10. Pipet 25 mℓ of H_2SO_4 (1+10, volume acid to volume water) to each ignition dish. While pipeting, carefully wash all traces of zinc oxide from the sides of the ignition dish.

11. Cover the ignition dish with a borosilicate (Pyrex) watch glass and warm the ignition dish on a hot plate until the zinc oxide is completely dissolved.

Note 12: Place the sample plus acid on the hot plate at a low heat Do not overheat or try to hasten the dissolution process. Allow 30 to 45 minutes for the dissolution.

12. Transfer the solution through filter paper to a 100 mℓ volumetric flask. Rinse the watch glass and the dish several times with distilled water (do not exceed 25 mℓ) and transfer the washings through the filter paper to the volumetric flask. The flask must be kept stoppered with a glass plug.

Note 13: The filtration usually requires a half hour. Use 12.5 cm filter paper to transfer the solution; this allows the transfer and the rinse to be made in one concerted step. In addition, it provides a good measure of the rinse water. Use a small orifice wash bottle. Wash the crucible, not the filter paper, because the P will be in solution.

13. Prepare the molybdate-hydrazine solution as described in subsection 2.2.4.3

14. Add 50 mℓ of the molybdate-hydrazine solution by pipet to each 100 mℓ volumetric flask. Mix immediately by swirling.

15. Dilute to 100 mℓ with water and mix well. Remove stoppers from flasks after mixing.

16. Place the 100 mℓ flasks in the constant-temperature bath for 25 minutes so that the contents of the falsks are below the liquid level of the bath. The temperature of the bath should be 82° to 88°C. See note 2.

17. Transfer the 100 mℓ flasks to the cooling bath and cool the contents rapidly to room temperature.

18. Replace stoppers and allow the samples to stand at room temperature for 15 minutes before measuring the absorbance.

Note 14: The color development is stable for at least 4 hours.

Note 15: The preparation of the samples and blank is critical in the determination of phosphorus in gasoline. The directions for the preparation of the samples and reagent blank must be followed to the

letter to insure accuracy in the resultant value of phosphorus. The importance of slowly delivering the samples of gasoline to the zinc oxide cannot be stressed enough.

19. Set the spectrophotometer to a wavelength of 820 nm. Allow at least 5 minutes for the spectrophotometer to warm up. If necessary, adjust the zero control to bring the meter needle to 0 on the percent absorbance scale. Standardize the radiation source by inserting 5 cm pathlength cells filled with distilled water into the sample and reference cell holders and by adjusting the radiation source as required until the meter reads 0 percent absorbance.

Note 16: Care must be taken that the sample and reference cells are not interchanged. In addition, each cell should be positioned reproducibly in the cell holder.

Note 17: The infrared absorption cells must be handled very carefully. Do not breathe onto or touch the window material with your fingers. By means of a hypodermic needle, transfer a portion of the liquid sample to the absorption cell. Wipe away any excess with a lint-free tissue or cloth. Place the cell in the sample compartment; close the cover.

20. Measure the absorbance of the reagent blank and, it is recommended, that of the standard sample (1.3 mg P/ℓ) before each set of determinations. Record the absorbance value of the reagent blank and the total µg P measured for the standard sample in the laboratory test record log book with the time to the nearest hour. If the absorbance of the reagent blank is within ±0.04 absorbance unit for a 5 cm cell of the calibration curve absorbance intercept and if the measured value of the standard sample is within ±0.4 µg P of the actual value, proceed to analyze the field samples. If the absorbance value of the blank is not within these limits, clean the glassware and rerun the test with fresh reagents. If the absorbance value of the standard sample is not within these limits, recalibrate the phosphorus calibration curve and check the complete absorbance scale with a calibrated set of filters from the National Bureau of Standards.

21. Measure the absorbance of the samples at the wavelength of maximum absorbance with distilled water in the reference cell.

22. Subtract the absorbance of the blank from the absorbance of each sample (note 5).

23. Record all measured values (i.e., reagent blanks, standard samples, samples) in sequential order in the laboratory test record log book. The date and time should be recorded with each set of determinations. The reagent blank should only be used with the set of determinations in which it was measured.

2.4 CALCULATIONS

Determine the micrograms of phosphorus in the sample using the calibration curve from subsection 2.2 and the corrected absorbance. Calculate the milligrams of phosphorus per litter of samples as follows:

$$\text{mg P/liter} = P/V$$

where P = total micrograms of phosphorus in the ignited sample, read from the calibration curve, and

V = total milliliters of ignited gasoline sample.

If the gasoline sample was taken at a temperature other than 15.6°C, make the following temperature correction:

$$\text{mg P/ℓ at } 15.6^{\circ}\text{C} = [\text{mg P/ℓ at t}]\ [1 + 0.001(t - 15.6)]$$

where t = observed temperature of the gasoline, °C.

The calculations are complete when the calculation data are recorded or a copy is filled in the Laboratory Test Record Log Book, shown in figure 6.

2.5 DATA REPORTING

Concentrations of phosphorus below 2.50 mg/ℓ should be reported to the nearest 0.01 mg/ℓ.

The concentration of phosphorus is to be recorded in the laboratory test record log book in the format shown in figure 6. The data reporting is not complete until the laboratory test record is filled out.

LABORATORY TEST RECORD

1. Test Station Sample Identification

   Test Station Sample Number:

   Region:

   Date of Station Test: ___/___/___
   MO DA YR

   Time of Station Test: ___:___
   HR MIN

2. Laboratory Identification

   Laboratory Name:

   Laboratory Address:

   Laboratory Analysis Number:

3. Test Information

   Date of Lab Test: ___/___/___
   MO DA YR

   Time of Lab Test: ___:___
   HR MIN

   P, mg/ℓ : __.__

4. Laboratory Technician

   Name:

   Signature:

   Date:

Figure 6. Laboratory test record

2.6 PHOSPHORUS CONTENT EQUALS OR EXCEEDS FEDERAL STANDARD

If the determined value of phosphorus in the field sample equals o exceeds the value promulgated in the Federal Register, 1.3 mg P/t, analyze the phosphorus content of a reference sample supplied by the supervisor. Concomitant with this analysis, analyze the phosphorus content of a second aliquot of the field sample which exceeded the Federal standard. Both analyses should be performed simultaneously according to the instructions in subsection 2.3.3. When the analyses are completed, report the results to your supervisor.

SECTION III QUALITY ASSURANCE PROCEDURES

3.0 GENERAL

The control of data quality is a function of two related activities of the quality assurance program: (1) development of standard operating procedures including control limits, and (2) assurance of conformance to the procedures and control limits. Standard operating procedures and control limits are recommended in the operations manual of this document. It is emphasized that if the analyst conscientiously adheres to the procedures and checks of section II, then the precision and accuracy of the phosphorus determinations should be within acceptable limits. Assurance of data quality basically involves collecting the information necessary to document and demonstrate the quality of the measured data. This section of the document will discuss the activities necessary to document and demonstrate data quality.

Verification of data quality is important in this instance because the data generated by this method are to be used to determine if the standard for phosphorous in gasoline is being met. If results indicate that the standard is being exceeded the appropriate enforcement group will be required to take action. Thus, the professional competence of the analyst, the operating procedures used, and the measured values that he reports may be challenged in a court of law.

The quality assurance procedures presented in this section should be carried out or closely monitored by the individual directly responsible for the quality of the reported data. In each laboratory one individual should be assigned the responsibility for quality assurance. With the exception of the independent audit, all functions could be performed by the analyst, if he is properly trained.

The purposes of this section are to:

1. Present information relative to the determination method (i.e., a functional analysis) to identify the important operations and factors,
2. Present techniques for the collection of information to identify trouble,

3. Present an independent performance audit procedure for use in quantifying data quality on an interlaboratory basis,
4. Present techniques for data quality assessment.

These four purposes will be discussed in the order stated in the subsections that follow. The first subsection (3.1) will contain a functional analysis of the determination method with the objective of identifying the most important factors that affect the quality of the reported data and of estimating the expected variation and biases in the measurements resulting from equipment and analyst errors.

Subsection 3.2 will contain suggestions for the collection and analysis of information to identify trouble. This will involve the use of control charts for the duplicate measurement of gasoline samples and for measurement of standard samples with appropriate criteria for decision making concerning whether the operation is in control and should be left alone or if it is out of control and corrective action is required.

Subsection 3.3 contains a discussion of an independent performance audit. Such an audit involves randomly inserting reference samples (i.e., NBS or otherwise certified samples) into the determination process. Such an audit, if feasible, could serve as an independent check of the determination process from sample handling through the final calculations. It would provide a means of assessing data quality as a function of bias and precision and serve as an independent verification of data quality for future users of the data.

Data quality assessment is discussed in subsection 3.4. A method for estimating the precision and accuracy of the reported data using the results from the independent performance audit is given. Also, a method of testing the quality against given standards using sampling by variables is given.

3.1 FUNCTIONAL ANALYSIS OF THE DETERMINATION METHOD

The determination of phosphorus in gasoline requires a sequence of operations and measurements that yields, as an end result, a number that serves to represent the mass of phosphorus in a unit volume of gasoline. The degree of agreement between the determined and the true value of a sample can be estimated from the agreement between determined and known or accepted values of reference samples. Precision and accuracy of the determination process are reduced to and/or maintained within acceptable limits by identifying and, where feasible, eliminating systematic errors. The importance of a variable on the precision and/or accuracy of a measurement process is a function of the variable's mean value and variance, how it is related to the dependent variable, and its probability of occurrence under normal operating conditions.

The objectives of this subsection are to:

1. Evaluate variables and estimate error ranges,
2. Determine, through a variance analysis, the variability to expect in the phosphorus in gasoline determinations,
3. Estimate, through a bias analysis, the expected bias, if any, in phosphorus in gasoline determinations.

A functional analysis of the determination process is performed to determine all the operations and variables that may affect the quality of the reported measurements. Data quality is characterized by measures of precision and bias. In subsection 3.1.1 variables believed to be important to the determination method are discussed. Estimates of the mean, variance, and probability distribution are made using data from published reports when available, and using engineering judgments when documented data are not available. These data are then used in a variance analysis (subsection 3.1.2) to determine the resulting variability of the measured value i.e., the mass of phosphorus per unit volume of gasoline. The data from subsection 3.1.1 are

also used in subsection 3.1.3 to estimate the potential bias of the determination process.

3.1.1 Variables Evaluation and Error Range Estimates

The milligrams of phosphorus per liter of sample at 15.6°C is calculated from the following relationship

$$P_c = [P_m/V]\ [1 + 0.001(t - 15.6)] \qquad (1)$$

where P_c = the concentration of phosphorus in gasoline at 15.6°C, mg/ℓ.

P_m = mass of phosphorus in the aliquot of gasoline sample as read from calibration curve at t°C, μg P.

V = volume of the gasoline sample at t°C, mℓ

t = temperature of the gasoline sample at analysis, °C.

Error sources then can be grouped according to whether they affect the determination of total mass of phosphorus, P_m, or the volume of the gasoline sample, V.

3.1.1.1 Potential Errors in Determining the Sample Volume, V. A sample, at the time it is collected, will contain a specific but unknown quantity of phosphorus per unit volume. The difference in the phosphorus content of the sample at the time of collection and that determined at some later time is due to error in the determination process. Following a hypothetical unit of volume of gasoline from collection through analysis, the following operations and/or measurements could, if not properly controlled, adversely influence the measurement results.

1. Evaporation during shipping and handling.
2. Measurement error in the 10 mℓ aliquot for analysis.
3. Evaporation losses while delivering the gasoline sample to the zinc oxide from a syringe.
4. Vaporization during the ignition process.
5. Incomplete transfer or loss of sample during filtering and rinse.

Of the potential errors listed above, error 1 would result in an apparent or measured volume smaller than the true volume, thus resulting in a higher than true measured phosphorus content. Errors 3, 4, and 5 would result in a lower than true phosphorus content. Error 2 would probably be randomly distributed about a zero mean value.

There are no data available for estimating the error associated with each of the above operations. However, a judgment can be made from the values given for repeatability and reproducibility of the method as written in the Federal Register (see appendix A).

For concentrations below 1.30 mg P/ℓ the repeatability and reproducibility of the determination method at the 95 percent confidence level are given as 0.05 mg P/ℓ and 0.13 mg P/ℓ, respectively. The above values mean that, on the average, duplicate results should agree within 0.05 mg P/ℓ 95 percent of the time when the determination process is operating properly. Also, results of two laboratories determining the same sample should agree within 0.13 mg P/ℓ 95 percent of the time when both laboratory determination processes are in control.

It is felt that at least half of the difference in the repeatability and reproducibility values is due to variability in analyst technique in performing the above listed operations.

3.1.1.2 Potential Errors in Determining Total Phosphorus, P. The quantity of phosphorus in a sample at the time of collection can differ from the determined value due to:

1. Contamination during sample handling and analysis,
2. Incomplete color development from the use of poor reagents and/or inadequate temperature control during color development,
3. Error in the calibration curve,
4. Imprecision of the spectrophotometer, including reading errors.

These sources of variability are estimated to account for less than half of the total determination process variability. The errors introduced by items (3) and (4) over a long period of time would tend to be randomly distributed about a zero mean. Incomplete color development acts as a negative bias, and sample contamination would act as a positive bias.

3.1.2 Variance Analysis

Many different factors may contribute to the variability of a determination method, for example:

1. The analyst,
2. Apparatus and reagents used,
3. Equipment calibration,
4. The environment (temperature, humidity, pollutant concentration, etc.).

The variability will be larger when the determinations to be compared are performed by different analysts and/or with different equipment than when they are carried out by a single analyst using the same equipment. Many different measures of variability are conceivable according to the circumstances under which the determinations are performed.

Only two extreme situations will be discussed here. They are:

1. Repeatability, r, is the value below which the absolute difference between duplicate results made on the same sample by the same analyst using the same equipment over a short interval of time may be expected to fall with a 95 percent probability.
2. Reproducibility, R, is the value below which the absolute difference between two determinations made on the same sample by different analysts in different laboratories using different equipment may be expected to fall with a 95 percent probability.

The above definitions are based on a statistical model according to which each determination is the sum of three components:

$$P_c = \bar{P} + b + e \qquad (2)$$

where

P_c = the measured value, mg P/ℓ,

$\bar{P}$ = the general average, mg P/ℓ,

b = an error term representing the differences between laboratories, mg P/ℓ,

e = a random error occurring in each determination, mg P/ℓ.

In general, b can be considered as the sum

$$b = b_r + b_s \qquad (3)$$

where b_r is a random component and b_s a systematic component. The term b is considered to be constant during any series of determinations performed under repeatability conditions, but to behave as a random variate in a series of determinations performed under reproducibility conditions. Its variance will be denoted as

$$\text{var } b = \sigma_L^2 , \tag{4}$$

the between-laboratory variance including the between-analyst and between-equipment variabilities.

The term, e, represents a random error occurring in each determination. Its variance

$$\text{var } e = \sigma_r^2$$

will be called the repeatability variance.

For the above model the repeatability, r, and the reproducibility, R, are given by

$$r = 1.96 \sqrt{2}\, \sigma_r = 2.77\, \sigma_r \tag{5}$$

and

$$R = 2.77\sqrt{\sigma_r^2 + \sigma_L^2} = 2.77\, \sigma_R . \tag{6}$$

where σ_R^2 will be referred to as the reproducibility variance.

Values of σ_r and σ_R can be obtained from the values of repeatability and reproducibility respectively as given for the reference method in the Federal Register (see appendix A). The repeatability, r, is given as 0.05 mg P/ℓ for concentrations below about 1.3 mg P/ℓ. Using this value in equation (5) gives σ_r = 0.018 mg P/ℓ. Reproducibility is given as R = 0.13 mg P/ℓ then from equation (6) σ_R = 0.047 mg P/ℓ.

As can be seen the reproducibility standard deviation is larger by almost a factor of 3 than the repeatability standard deviation. It is felt this large difference is due primarily to differences in analyst techniques for performing the operations (listed in subsection 3.1.1.1) contributing to the variability in determining the true sample volume. From equation (1) the

coefficient of variation of P_c is given by

$$CV\{P_c\} = \sqrt{CV^2\{P_m\} + CV^2\{V\}} \qquad (7)$$

and the standard deviation then is

$$\sigma\{P_c\} = CV\{P_c\} \times P_c .$$

From the discussion in subsection 3.1.1.2, it can be assumed that for repeatability conditions the variability in determining the total phosphorus content in a gasoline sample in mg P/ℓ is primarily due to the variability in the spectrophotometer. This should be relatively small, say on the order of $\sigma\{P_m\} = 0.1$ µg P. Then taking $\sigma\{P_c\} = \sigma_r = 0.018$ mg P/ℓ and using values of $P_c = 1.3$ mg P/ℓ, $P_m = 13$ µg P and V = 10 ml, equation (7) gives

$$CV\{V\} = 0.012 ,$$

and at V = 10 ml,

$$\sigma\{V\} = 0.12 \text{ ml} .$$

If the above assumptions are reasonable, then it is obvious that control actions should be directed toward the operations listed in subsection 3.1.1.1 as the most effective means of controlling and assuring data of acceptable quality.

3.1.3 Bias Analysis

There are no data available for estimating the bias of the determination process. However, most of the error sources listed in the previous subsections act as positive biases. Therefore, it would seem reasonable to assume that in general, the determined results will be higher than the actual values. The bias could be evaluated by measuring reference samples if and when they become available.

Assuming that the true or acceptable value, P_T, of a sample is known, then from equation (2)

$$\bar{P} - P_T = \tau \qquad (8)$$

which represents the bias of the determination method. An estimate of the bias can be obtained from audit results as discussed in section 3.3.

3.2 COLLECTION OF INFORMATION TO IDENTIFY TROUBLE

In a quality assurance program, one of the most effective means of preventing trouble is to respond immediately to indications of suspicious data or equipment malfunctions. Certain visual and operational checks can be performed by the analyst while the measurements are being made to help insure the generation of data of acceptable quality. These checks are written as part of the routine operating procedures in section II.

The use of control charts is recommended as a method for monitoring and documenting the performance level of the determination process. Recommended quality control charts are:

1. A control chart for duplicate results to monitor analyst technique and equipment stability,
2. A control chart for the determination of standard solutions to monitor calibration stability.

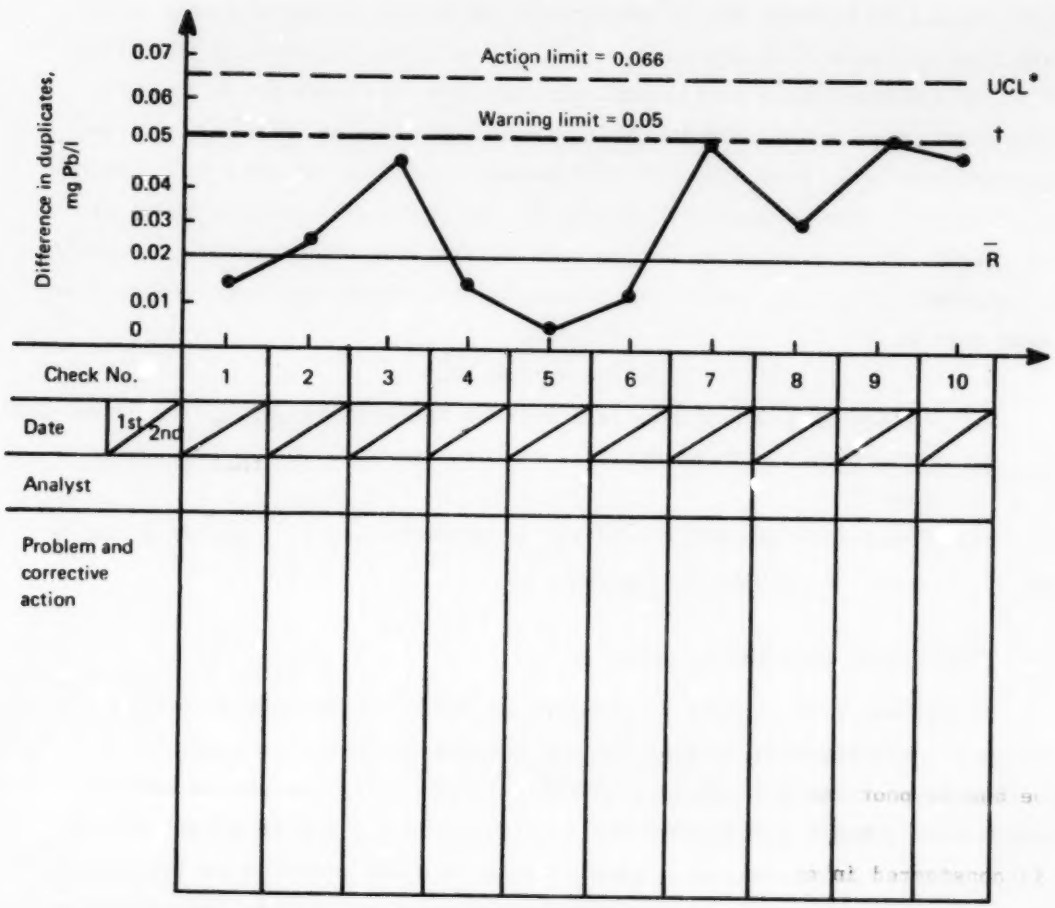
A sample control chart for each of the above parameters with suggested limits is given in the following subsections. Control charts are discussed in textbooks, such as refs. 11 and 12.

3.2.1 Control Chart for Duplicates

A sample control chart for the difference in duplicate measurements of a gasoline sample is given in figure 7. It is recommended that a duplicate determination be made once a week or once for every 40 samples analyzed, whichever occurs first. The second determination should be separated by at least 2 days or 20 samples from the original determination.

Take the absolute difference in the duplicates and plot the point on the graph of figure 7. Connect each point to the previously plotted point by a straight line. A point falling outside the UCL indicates that an actual change has occurred in the determination process. Such a change could be due to poor technique, equipment change, and/or sample deterioration. As long as the plotted points remain within the UCL, the determination process is considered in control and no action is required.

When a point falls outside the UCL, a quick check would be to prepare and measure a standard sample of about the same absorbance to check the phosphorus calibration curve. If the calibration curve has not changed, the



* $\underline{U}CL = \bar{R} + 3d_3 \sigma_r = 0.02 + 3(0.853)(0.018) = 0.066$
† $\bar{R} = d_2 \sigma_r = 1.128 \times 0.018 = 0.02$

Figure 7. Sample quality control chart for duplicate determinations of gasoline samples.

most likely cause of the excess variability is poor technique. The sample should be measured again after reviewing the analysis procedures. Plot the difference in the original and third determinations and if it is below the UCL continue the operation.

3.2.2 Control Chart for Standard Samples

Duplicate determinations of a standard sample should agree closer than duplicate determinations of a gasoline sample because a major portion of variability due to analyst technique is eliminated. The calibration curve should be suspect if the determined value of a standard sample differs more than 0.4 µg P from its known value. This value is taken as the action limit in constructing a sample control chart for the differences in the determined value and the known value of standard samples (fig. 8). As each standard sample is determined the difference should be computed and plotted on the graph. Each point is connected to the previously plotted point with a straight line. Corrective action such as cleaning the glassware, preparing new standard solutions, and/or recalibrating the spectrophotometer should be taken anytime:

1. One point falls outside the action limits.
2. Two out of three points fall between the warning and action lines, and
3. Seven consecutive points fall on the same side of the average or zero line.

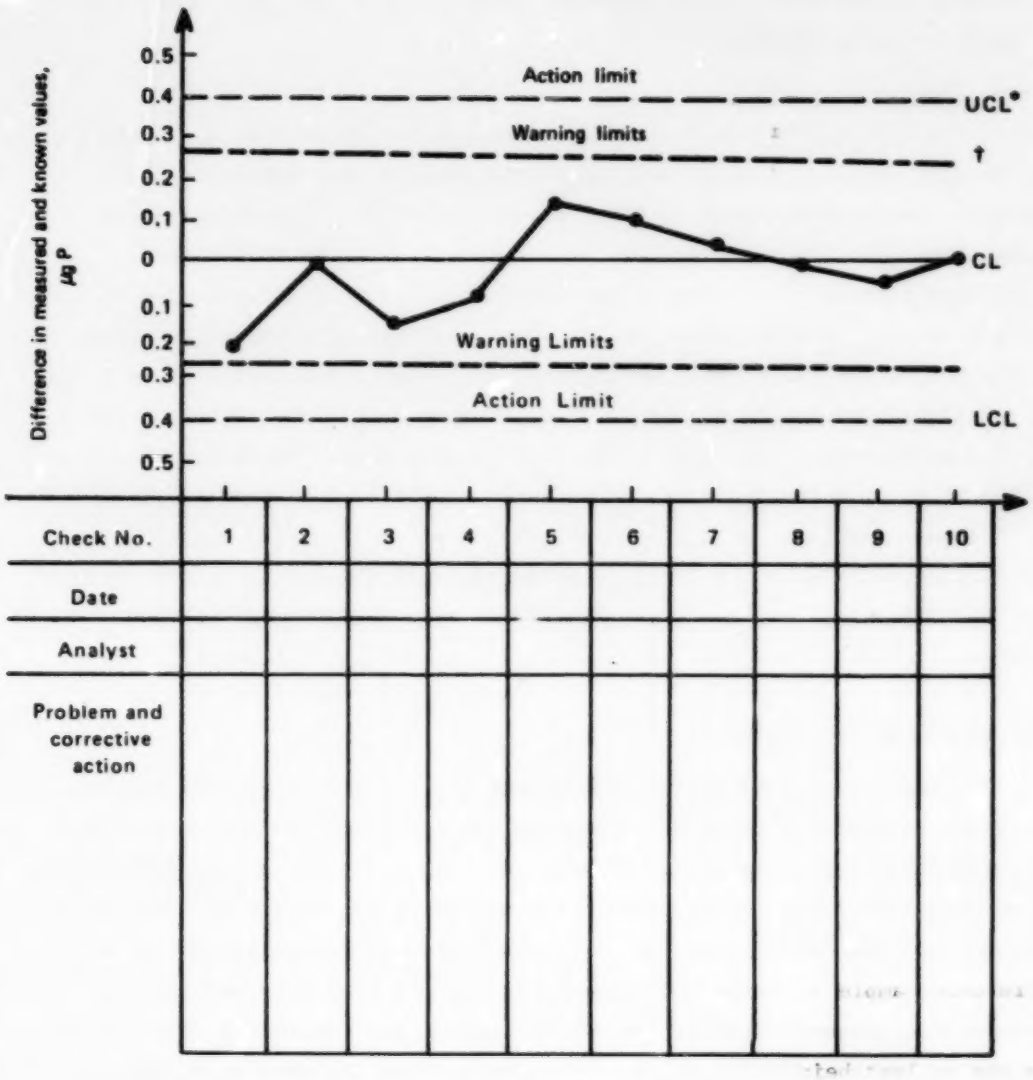
Analysis of gasoline samples should not be attempted until a atandard sample can be measured to within ±0.4 µg P.

3.3 INDEPENDENT PERFORMANCE AUDIT

If implemented properly an independent audit can be used to evaluate the total determination process through the use of reference samples. A reference sample is defined as a gasoline sample whose phosphorus content is accurately known (preferably NBS certified) to the auditors but unknown to the analyst being audited. Results from an audit provides an independent assessment of data quality by providing a means of estimating the precision and bias of the reported results.

3.3.1 Procedure for Performing A Quality Audit

The individual or organization responsible for performing the audit should obtain a supply of gasoline samples with known phosphorus concentrations.



* UCL = 3σ = 0.04 µg P (estimated, not derived from actual data)
† Warning Limit = 2σ = 2.7

Figure 8. Sample control chart for the determination of standard samples.

Samples should be placed in sample containers identical to the containers used in the field. If possible the reference sample should not be distinguishable from regular field samples. These reference samples should be shipped or delivered to the analysis laboratory in the same manner that is used for field samples.

3.3.2 Frequency of Audit

The optimum frequency of audit is a function of certain costs and the desired level of confidence in the data quality assessment. Also, another consideration would have to be the quality of the data presently being reported. The repeatability and reproducibility of this method appear small enough to indicate that precision of the method will not be a big problem. However, there are no data available to estimate the bias of the method and this could be important to the accuracy of the reported data.

Initially an auditing level of a minimum of once a week or everytime a field sample exceeds the Federal standard is required. For an analyst analyzing about 8 samples a day, this would result in a minimum of 13 audits per calendar quarter. If the data for the first audit period indicate that only good quality data are being reported the auditing level could be reduced but probably should not be lower than six to seven audits per calendar quarter.

3.4 DATA QUALITY ASSESSMENT

Two aspects of data quality assessment are considered in this section. The first considers a means of estimating the precision and accuracy of the reported data, e.g., reporting the bias, if any, and the standard deviation associated with the determinations. The second consideration is that of testing the data quality against given standards using sampling by variables. For example, lower and upper limits, L and U, may be selected to include a large percentage of the determinations and outside of which it is desired to control the percentage of determinations to, say, less than 10 percent. If the data quality is not consistent with these limits, L and U then, action is taken to correct the possible deficiency as quickly as possible and to correct the previous data when possible and/or feasible.

3.4.1 Estimating the Precision/Accuracy of the Reported Data

This section will indicate how the audit data collected in accordance with the procedure described in section 3.3.1 will be utilized to estimate the precision and accuracy of the determination of interest. Similar techniques can also be used by a specific firm or laboratory to assess their or its own determinations. The audit data collected as a result of following the procedures in the previous section are the determined and known values of P_c and the difference.

$$d_j = P_{cj} - P_{aj}$$

where P_{cj} = Determined value of phosphorus in the reference sample, mg P/ℓ,

P_{aj} = Known value of phosphorus in the reference sample, mg P/ℓ, and

j = the audit number, $j = 1, \ldots n$.

Let the mean and standard deviation of the differences d_j, $j = 1, \ldots n$ audits be denoted by $\bar{d}$ and s_d, respectively. Thus,

$$\bar{d} = \sum_{j=1}^{n} d_j/n,$$

and

$$s_d = \left[\sum_{j=1}^{n} (d_j - \bar{d})^2/(n-1)\right]^{1/2}.$$

3.4.2 Statistical Tests

The mean $\bar{d}$ is an estimate of the relative bias in the determinations (i.e., relative to the known or accepted value). Assuming the audit value to be unbiased, the existence of a bias in the laboratory data can be checked by the appropriate t-test, i.e.,

$$t_{n-1} = \frac{\bar{d} - 0}{s_d/\sqrt{n}}.$$

See ref. 13 for a discussion of the t-test. If t is significantly large in absolute values, i.e., greater than the tabulated value of t with

n - 1 degrees of freedom, which is exceeded by chance only 5 percent of the time, then the bias is considered to be real and some check should be made for a possible cause of the bias. If t is not significantly large, then the bias should be considered zero or negligible. However, its calculated value will be reported with the laboratory data for that audit period.

The standard deviation, s_d, is a function of both the standard deviation of the laboratory determinations and of precision with which the reference sample value is known. Assuming the reference sample values are known with much greater precision than the laboratory determinations, then the calculated s_d is an estimate of the standard deviation of the laboratory determination. Table 2, contains an example calculation of $\bar{d}$ and s_d, starting with the differences for a sample size of n = 12.

The calculated standard deviation can then be utilized to check the reasonableness of the assumption made in subsection 3.1.2 concerning $\sigma\{P_c\} = \sigma_R = 0.047$ mg P/ℓ, under reproducibility conditions. The calculated standard deviation, s_d, may be directly checked against the assumed value, σ_R, by using the statistical test procedure

$$\frac{\chi^2}{f} = \frac{s_d^2}{\sigma^2\{P_c\}}$$

where χ^2/f is the value of a random variable having the chi-square distribution with f = n - 1 degrees of freedom. If χ^2/f is larger than the tabulated value exceeded only 5 percent of the time, then it would be concluded that the test procedure is yielding results with more variability than is acceptable due to some assignable cause of large variation.

The determined values should be reported along with the estimated bias, $\bar{d}$, standard deviation, s_d, the number of audits, n, and the total number of determination periods (number of days analyses were performed) N, sample ($n \leq N$). Estimates, i.e., s_d and $\bar{d}$, which are significantly different

from the assumed population parameters should be identified on the data sheet. For example, based on the data of table 2, if the analyst reported a value of P_c = 1.30 mg P/ℓ for one of the N field tests not audited, then that determination would be reported as

1. Determined value, P_c = 1.30 mg P/ℓ
2. Calculated bias, $\bar{d} = \hat{\tau}$ = -0.133 mg P/ℓ
3. Calculated standard deviation, $\hat{\sigma}\{P_c\} = s_d$ = 0.12 mg P/ℓ
4. Auditing level, n = 12, N = 65.

From the above data, users of the data can calculate confidence limits appropriate to what the data are to be used for.

The t-test and χ^2-test described above are used to check on the biases and standard deviations separately. In order to check on the overall data quality as determined by the percent of determination deviations outside prescribed limits, it is necessary to use the approach described below.

3.4.3 Sampling by Variables

Because the lot size (i.e., the number of determination periods during a particular period, normally a calendar quarter) is small, N = 65, and consequently, the sample size is small on the order of n = 13, it is important to consider a sampling by variables approach to assess the data quality with respect to prescribed limits. That is, it is desired to make as much use of the data as possible. In the variables approach, the means and standard deviations of the sample of n audits are used in making a decision concerning the data quality.

Some background concerning the assumptions and the methodology is repeated below for convenience. However, one is referred to one of a number of publications having information on sampling by variables; e.g., see refs. 13-17. The discussion below will be given in regard to the specific problem herein which has some unique features as compared with the usual variable sampling plans.

The difference between the analyst-determined and the known value of P_c is designated as d_j, and the mean difference over n audits by $\bar{d}$, that is,

Table 2. Computation of mean difference, $\bar{d}$, and standard deviation of differences, s_d

General Formulas $d = P_{dj} - P_{aj}$		Specific Example Data (mg P/ℓ)	
d_1	d_1^2	-0.05	0.0025
d_2	d_2^2	-0.02	0.0004
d_3	d_3^2	0.00	0.0000
d_4	d_4^2	-0.03	0.0009
d_5	d_5^2	-0.06	0.0036
d_6	d_6^2	0.01	0.0001
d_7	d_7^2	0.02	0.0004
d_8	d_8^2	-0.03	0.0009
d_9	d_9^2	-0.04	0.0016
d_{10}	d_{10}^2	0.01	0.0001
d_{11}	d_{11}^2	-0.03	0.0009
d_{12}	d_{12}^2	0.00	0.0000
Σd_j	Σd_j^2	-0.16	0.0114
$\bar{d} = \Sigma d_j / n$		$\bar{d} = -0.133$	
$s_d^2 = \frac{\Sigma d_j^2 - (\Sigma d_j)^2/n}{n-1}$		$s_d^2 = 0.01463$	
$s_d = \sqrt{s_d^2}$		$s_d = 0.12$ mg P/ℓ	

$$\bar{d} = \frac{1}{n} \sum_{j=1}^{n} \left(P_{c_j} - P_{a_j} \right).$$

Theoretically, P_{c_j} and P_{a_j} should be measures of the same phosphorous concentration, and their difference should have a mean of zero on the average. In addition, their differences should have a standard deviation approximately equal to that associated with determinations of P_c separately.

Assuming three standard-deviation limits (using the assumed $\sigma\{P_c\}$ = 0.047 mg P/ℓ as derived in the variance analysis of subsection 3.1.2), the values -3(0.047) = 0.141 mg P/ℓ and 3(0.047) = 0.141 mg P/ℓ define lower and upper limits, L and U, respectively, outside of which it is desired to control the proportion of differences, d_j. Following the method given in ref. 14, a procedure for applying the variables sampling plan is described below. Figures 9 and 10 illustrate examples of satisfactory and unsatisfactory data quality with respect to the prescribed limits L and U.

The variables sampling plan requires the sample mean difference, $\bar{d}$; the standard deviation of these differences, s_d; and a constant, k, which is determined by the value of p, the proportion of the differences outside the limits of L and U. For example, if it is desired to control at 0.10 the probability of not detecting lots with data quality p equal to 0.10 (or 10 percent of the individual differences outside L and U) and if the sample size n = 12, then the value of k can be obtained from table 2 of ref. 14. The values of $\bar{d}$ and s_d are computed in the usual manner; see table 2 for formulas and a specific example. Given the above information, the test procedure is applied and subsequent action is taken in accordance with the following criteria:

1. If both of the following conditions are satisfied:

$$\bar{d} - k\, s_d \geq L = -0.141 \text{ mg P/ℓ}$$

$$d + k\, s_d \leq U = 0.141 \text{ mg P/ℓ}$$

the individual differences are considered to be consistent with the prescribed data quality limits and no corrective action is required.

2. If one or both of these inequalities is violated, possible deficiencies exist in the determination process as carried out for that

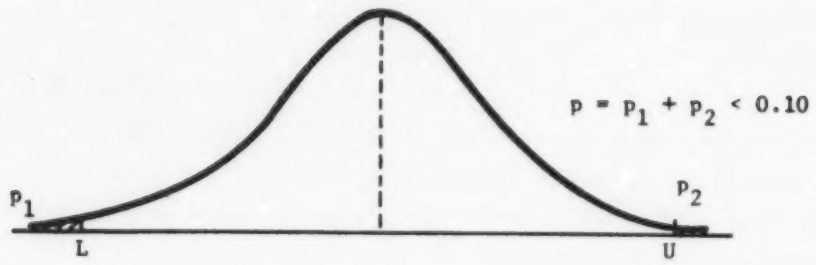


Figure 9. Example Illustrating p < 0.10 and Satisfactory Data Quality.

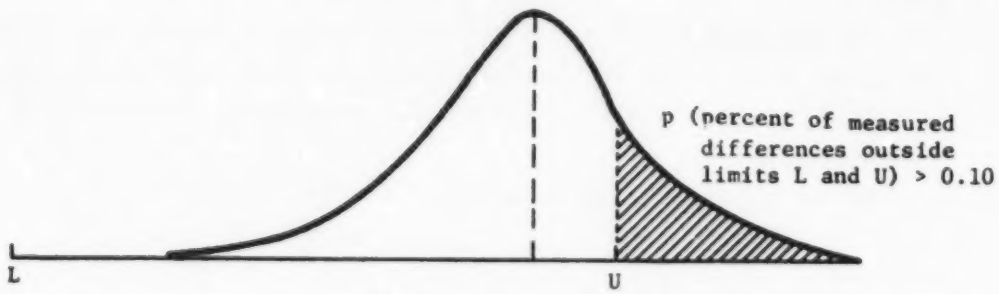


Figure 10. Example illustrating p > 0.10 and unsatisfactory data quality.

particular lot (group) of determination periods. These deficiencies should be identified and corrected as soon as possible to prevent future determinations of unacceptable quality. Data corrections should be made when possible, i.e., if a quantitative basis is determined for correction.

Table 3 contains a few selected values of n, p, and k for convenient reference.

Using the values of $\bar{d}$ and s_d in table 2, k = 2.045 for a sample size n = 12, and p = 0.10 (table 3), the test criteria can be checked; i.e.,

$$\bar{d} - k\, s_d = -0.133 - (2.045)(0.12) = -0.38 < L = -0.141 \text{ mg P/}\ell$$

$$\bar{d} + k\, s_d = 0.133 + (2.045)(0.12) = 0.112 < U = 0.141 \text{ mg P/}\ell$$

Therefore, both inequalities are not satisfied; specifically, the lower limit, L, has been exceeded; hence the data are not consistent with the limits. The laboratory responsible for generating these data should be notified to increase its quality control activities. The calendar quarter of data or a portion of that quarter of data should be invalidated only if one or more of the reported determinations approached, within determination error, or exceeded, the standard.

The above plan provides a 90 percent probability of detecting lots with 10 percent or more defects (i.e., deviations falling outside the designated limits L and U).

Table 3. Sample plan constants, k for P{not detecting a lot with proportion p outside limits L and U} $\leq$ 0.1

Sample Size n	k(p = 0.2)	k(p = 0.1)
3	3.039	4.258
5	1.976	2.742
7	1.721	2.334
10	1.595	2.112
12	1.550	2.045
13	1.533	2.02
14	1.519	1.999
15	1.506	1.981

SECTION IV REFERENCES

1. "Standard Method of Test for Phosphorous in Gasoline," American Society for Testing and Materials, Method D 3231-73 (1973).
2. M. G. Mellon and R. E. Kitson. Ind. Eng. Chem., Anal. Ed. 16, 466 (1944).
3. M. E. Griffing et al. Anal. Chem. 32, 374 (1960).
4. I. M. Kolthoff et al. Quantitative Chemical Analysis, 4th ed. Toronto, Ontario: The MacMillan Co., 1969.
5. F. D. Snell and C. T. Snell. Colorimetric Methods of Analysis, 3rd ed., Vol. II. New York: Van Nostrand, 1949, pp. 630-81.
6. D. F. Boltz and M. G. Mellon. Anal. Chem. 19, 873 (1947).
7. H. H. Willard and L. J. Center. Ind. Eng. Chem., Anal. Ed. 13, 81 (1941).
8. J. R. Woods and M. G. Mellon, Ibid., 13, 760 (1941).
9. Natl. Bur. Std. Circ. 434, 1941; 602, 1959.
10. H. H. Willard et al. Instrumental Methods of Analysis, 4th ed. New York: D. Van Nostrand Co., Inc., 1965, p. 153.
11. E. L. Grant and R. S. Leavenworth. Statistical Quality Control, 4th ed. St. Louis: McGraw-Hill, 1972.
12. D. A. Simons. Practical Quality Control. Reading, Mass.: Addison-Wesley Publishing Company, 1970. pp. 131-150.
13. A. Hald. Statistical Theory with Engineering Applications. New York: John Wiley and Sons, 1952.
14. D. B. Owen. "Variables Sampling Plans Based on the Normal Distribution." Technometrics 9, No. 3 (August 1967).
15. D. B. Owen. "Summary of Recent Work on Variables Acceptance Sampling with emphasis on Non-normality." Technometrics 11 (1969):631-37.
16. Kinji Takogi. "On Designing Unknown Sigma Sampling Plans Based on a Wide Class of Non-Normal Distributions." Technometrics 14 (1972): 669-78.
17. C. Eisenhart, M. Hastay, and W. A. Wallis, eds. Techniques of Statistical Analysis. Statistical Research Group, Columbia, University. New York: McGraw-Hill, 1947.

APPENDIX A TEST FOR THE DETERMINATION OF PHOSPHORUS IN GASOLINE

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APPENDIX A

TEST FOR THE DETERMINATION OF PHOSPHORUS IN GASOLINE

1. *Scope.* 1.1 This method was developed for the determination of phosphorus generally present as pentavalent phosphate esters or salts, or both, in gasoline. This method is applicable for the determination of phosphorus in the range from 0.0008 to 0.15 g P/U.S. gal, or 0.2 to 40 mg P/litre.

2. *Applicable documents.* 2.1 ASTM Standards:

D 1100 Specification for Filter Paper for Use in Chemical Analysis.

3. *Summary of method.* 3.1 Organic matter in the sample is decomposed by ignition in the presence of zinc oxide. The residue is dissolved in sulfuric acid and reacted with ammonium molybdate and hydrazine sulfate. The absorbance of the "Molybdenum Blue" complex is proportional to the phosphorus concentration in the sample and is read at approximately 820 nm in a 5-cm cell.

4. *Apparatus.* 4.1 Buret, 10-ml capacity, 0.05-ml subdivisions.

4.2 Constant-Temperature Bath, equipped to hold several 100-ml volumetric flasks submerged to the mark. Bath must have a large enough reservoir or heat capacity to keep the temperature at 180 to 190° F (82.2 to 87.8° C) during the entire period of sample heating.

NOTE 1: If the temperature of the hot water bath drops below 180° F (82.2° C) the color development may not be complete.

4.3 Cooling Bath, equipped to hold several 100-ml volumetric flasks submerged to the mark in ice water.

4.4 Filter Paper, for quantitative analysis, Class G for fine precipitates as defined in Specification D 1100.

4.5 Ignition Dish—Coors porcelain evaporating dish, glazed inside and outside, with pourout (size no. 00A, diameter 75mm, capacity 70 ml).

4.6 Spectrophotometer, equipped with a tungsten lamp, a red-sensitive phototube capable of operating at 830 nm and with absorption cells that have a 5-cm light path.

4.7 Thermometer, range 50 to 200° F (10 to 105° C).

4.8 Volumetric Flask, 100-ml with ground-glass stopper.

4.9 Volumetric Flask, 1000-ml with ground-glass stopper.

4.10 Syringe, Luer-Lok, 10-ml equipped with 5-cm, 22-gage needle.

5. *Reagents.* 5.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity.

5.3 Ammonium Molybdate Solution—Using graduated cylinders for measurement add slowly (Note 2), with continuous stirring, 225 ml of concentrated sulfuric acid to 800 ml of water contained in a beaker placed in a bath of cold water. Cool to room temperature and add 20 g of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$). Stir until solution is complete and transfer to a 1000-ml flask. Dilute to the mark with water.

NOTE 2: Wear a face shield, rubber gloves, and a rubber apron when adding concentrated sulfuric acid to water.

5.4 Hydrazine Sulfate Solution—Dissolve 1.5 of hydrazine sulfate ($H_2NNH_2\cdot H_2SO_4$) in 1 litre of water, measured with a graduated cylinder.

NOTE 3: This solution is not stable. Keep it tightly stoppered and in the dark. Prepare a fresh solution after 3 weeks.

5.5 Molybdate-Hydrazine Reagent—Pipet 25 ml of ammonium molybdate solution into a 100-ml volumetric flask containing approximately 50 ml of water, add by pipet 10 ml of $N_2NNH_2\cdot H_2SO_4$ solution, and dilute to 100 ml with water.

NOTE 4: This reagent is unstable and should be used within about 4 h. Prepare it immediately before use. Each determination (including the blank) uses 50 ml.

5.6 Phosphorus, Standard Solution (10.0 μg P/ml)—Pipet 10 ml of stock standard phosphorus solution into a 1000-ml volumetric flask and dilute to the mark with water.

5.7 Phosphorus, Stock Standard Solution (1.00 mg P/ml)—Dry approximately 5 g of potassium dihydrogen phosphate (KH_2PO_4) in an oven at 221 to 230° F (105 to 110° C) for 2 h. Dissolve 4.393±0.003 g of the reagent in 150 ml, measured with a graduated cylinder, of H_2SO_4 (1+10) contained in a 1000-ml volumetric flask. Dilute with water to the mark.

5.8 Sulfuric Acid (1+10)—Using graduated cylinders for measurement add slowly (Note 2), with continuous stirring, 100-ml of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 1 litre of water contained in a beaker placed in a bath of cold water.

5.9 Zinc Oxide.

NOTE 5: High-bulk density zinc oxide may cause spattering. Density of approximately 0.5 g/cm³ has been found satisfactory.

6. *Calibration.* 6.1 Transfer by buret, or a volumetric transfer pipet, 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 3.5, and 4.0 ml of phosphorus standard soultion into 100-ml volumetric flasks.

6.2 Pipet 10 ml of H_2SO_4 (1+10) into each flask. Mix immediately by swirling.

6.3 Prepare the molybdate-hydrazine solution. Prepare sufficient volume of reagent based on the number of samples being analyzed.

6.4 Pipet 50 ml of the molybdate-hydrazine solution to each volumetric flask. Mix immediately by swirling.

6.5 Dilute to 100 ml with water.

6.6 Mix well and place in the constant-temperature bath so that the contents of the flask are submerged below the level of the bath. Maintain bath temperature at 180 to 190°F (82.2 to 87.8°C) for 25 min (Note 1).

6.7 Transfer the flask to the cooling bath and cool the contents rapidly to room temperature. Do not allow the samples to cool more than 5°F (2.8°C) below room temperature.

NOTE 6: Place a chemically clean thermometer in one of the flasks to check the temperature.

6.8 After cooling the flasks to room temperature, remove them from the cooling water bath and allow them to stand for 10 min at room temperature.

6.9 Using the 2.0-ml phosphorus standard in a 5-cm cell, determine the wavelength near 820 nm that gives maximum absorbance. The wavelength giving maximum absorbance should not exceed 830nm.

6.9.1 Using a red-sensitive phototube and 5-cm cells, adjust the spectrophotometer to zero absorbance at the wavelength of maximum absorbance using distilled water in both cells. Use the wavelength of maximum absorbance in the determination of calibration readings and future sample readings.

6.9.2 The use of 1-cm cells for the higher concentrations is permissible.

6.10 Measure the absorbance of each calibration sample including the blank (0.0 ml phosphorus standard) at the wavelength of maximum absorbance with distilled water in the reference cell.

NOTE 7: Great care must be taken to avoid possible contamination. If the absorbance of the blank exceeds 0.04 (for 5-cm cell), check for source of contamination. It is suggested that the results be disregarded and the test be rerun with fresh reagents and clean glassware.

6.11 Correct the absorbance of each standard solution by subtracting the absorbance of the blank (0 ml phosphorus standard).

6.12 Prepare a calibration curve by plotting the corrected absorbance of each standard solution against micrograms of phosphorus. One millilitre of phosphorus standard solution provides 10 μg of phosphorus.

7. *Sampling.* 7.1 Selection of the size of the sample to be tested depends on the expected concentration of phosphorous in the sample. If a concentration of phosphorus is suspected to be less than 0.0038 g/gal (1.0 mg/litre), it will be necessary to use 10 ml of sample.

NOTE 8: Two grams of zinc oxide cannot absorb this volume of gasoline. Therefore the 10-ml sample is ignited in aliquots of 2 ml in the presence of 2 g of zinc oxide.

7.2 The following table serves as a guide for selecting sample size:

Phosphorus, milligrams per litre	Equivalent, grams per gallon	Sample size, millilitre
3.5 to 40	0.01 to 0.15	1.00
1.3 to 20	0.005 to 0.075	2.70
0.6 to 13	0.0037 to 0.05	3.00
1 or less	0.003s or less	10.00

8. *Procedure.* 8.1 Transfer 2±0.2 g of zinc oxide into a conical pile in a clean, dry, unetched ignition dish.

NOTE 9: In order to obtain satisfactory accuracy with the small amounts of phosphorus involved, it is necessary to take extensive precautions in handling. The usual precautions of cleanliness, careful manipulation, and avoidance of contamination should be scrupulously observed; also, all glassware should be cleaned before use, with cleaning acid or by some procedure that does not involve use of commercial detergents. These compounds often contain alkali phosphates which are strongly adsorbed by glass surfaces and are not removed by ordinary rinsing. It is desirable to segregate a special stock of glassware for use only in the determination of phosphorus.

8.2 Ma[illegible] a deep depression in the center of the z[illegible] oxide pile with a stirring rod.

8.3 Pipet the gasoline sample (Note 10) (see 7.2 for suggested sample volume) into the depression in the zinc oxide. Record the temperature of the fuel if the phosphorus content is required at 60° F (15.6° C) and make correction as directed in 9.2.

NOTE 10: For the 10-ml sample use multiple additions and a syringe. Hold the tip of the needle at approximately ⅓ of the depth of the zinc oxide layer and slowly deliver 2 ml of the sample: fast sample delivery may give low results. Give sufficient time for the gasoline to be absorbed by the zinc oxide. Follow step 8.6. Cool the dish to room temperature. Repeat steps 8.3 and 8.6 until all the sample has been burned. Safety—cool the ignition dish before adding the additional aliquots of gasoline to avoid a flash fire.

8.4 Cover the sample with a small amount of fresh zinc oxide from reagent bottle (use the tip of a small spatula to deliver approximately 0.2 g). Tap the sides of the ignition dish to pack the zinc oxide.

8.5 Prepare the blank, using the same amount of zinc oxide in an ignition dish.

8.6 Ignite the gasoline, using the flame from a bunsen burner. Allow the gasoline to burn to extinction (NOTE 10).

8.7 Place the ignition dishes containing the sample and blank in a hot muffle furnace set at a temperature of 1150 to 1300° F (621 to 704° C) for 10 min. Remove and cool the ignition dishes. When cool gently tap the sides of the dish to loosen the zinc oxide. Again place the dishes in the muffle furnace for 5 min. Remove and cool the ignition dishes to room temperature. The above treatment is usually sufficient to burn the carbon. If the carbon is not completely burned off place the dish into the oven for further 5-min. periods.

NOTE 11: Step 8.7 may also be accomplished by heating the ignition dish with a Meker burner gradually increasing the intensity of heat until the carbon from the sides of the dish has been burned, then cool to room temperature.

8.8 Pipet 25 ml of H_2SO_4 (1+10) to each ignition dish. While pipeting, carefully wash all traces of zinc oxide from the sides of the ignition dish.

8.9 Cover the ignition dish with a borosilicate watch glass and warm the ignition dish on a hot plate until the zinc oxide is completely dissolved.

8.10 Transfer the solution through filter paper to a 100-ml volumetric flask. Rinse the watch glass and the dish several times with distilled water (do not exceed 25 ml) and transfer the washings through the filter paper to the volumetric flask.

8.11 Prepare the molybdate-hydrazine solution.

8.12 Add 50 ml of the molybdate-hydrazine solution by pipet to each 100-ml volumetric flask. Mix immediately by swirling.

8.13 Dilute to 100 ml with water and mix well. Remove stoppers from flasks after mixing.

8.14 Place the 100-ml flasks in the constant-temperature bath for 25 min so that the contents of the flasks are below the liquid level of the bath. The temperature of the bath should be 180 to 190°F (82.2 to 87.8°C) (Note 1).

8.15 Transfer the 100-ml flasks to the cooling bath and cool the contents rapidly to room temperature (NOTE 6).

8.16 Allow the samples to stand at room temperature before measuring the absorbance.

NOTE 12: The color developed is stable for at least 4 h.

8.17 Set the spectrophotometer to the wavelength of maximum absorbance as determined in 8.9. Adjust the spectrophotometer to zero absorbance, using distilled water in both cells.

8.18 Measure the absorbance of the samples at the wavelength of maximum absorbance with distilled water in the reference cell.

8.19 Subtract the absorbance of the blank from the absorbance of each sample (NOTE 7).

8.20 Determine the micrograms of phosphorous in the sample, using the calibration curve from 8.12 and the corrected absorbance.

9. *Calculations.* 9.1 Calculate the milligrams of phosphorus per litre of sample as follows:

$$P, \text{ mg/litre} = P/V$$

where:

P = micrograms of phosphorus read from calibration curve, and

V = millilitres of gasoline sample.

To convert to grams of phosphorus per U.S. gallon of sample, multiply mg P/litre by 0.0038.

9.2 If the gasoline sample was taken at a temperature other than 60°F (15.6°C) make the following temperature correction:

$$\text{mg P/litre at 15.6°C} = [\text{mg P/litre at t}][1+0.001\ (t-15.6)]$$

where:

t = observed temperature of the gasoline, °C.

9.3 Concentrations below 2.5 mg/litre or 0.01 g/gal should be reported to the nearest 0.01 mg/litre or 0.0001 g/U.S. gal.

9.3.1 For higher concentrations, report results to the nearest 1 mg P/litre or 0.005 g P/U.S. gal.

10. *Precision.* 10.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

10.2 Repeatability—Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

g P/U.S. gal (mg P/litre)	*Repeatability*
0.0008 to 0.005 (0.2 to 1.3).	0.0005 g P/U.S. gal (0.13 mg P/litre),
0.005 to 0.15 (1.3 to 40)	13% of the mean.

10.3 Reproducibility—The results submitted by each of two laboratories should not be considered suspect unless they differ by more than the following amounts:

g P/U.S. gal (mg P/litre)	*Reproducibility*
0.0008 to 0.005 (0.2 to 1.3).	0.0002 g P/U.S. gal (0.05 mg P/litre).
0.005 to 0.15 (1.3 to 40)	7% of the mean.

Title 40—Protection of Environment

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

SUBCHAPTER C—AIR PROGRAMS

PART 80—REGULATIONS OF FUELS AND FUEL ADDITIVES

Lead and Phosphorus Test Procedures

Correction

In FR Doc. 74-15449 appearing at page 24890 in the issue of Monday, July 8, 1974, make the following changes:

1. On page 24891:

a. In the seventeenth line of the first paragraph in the first column, the word "result" should read "results".

b. In the first line of paragraph 4.7 in the third column, the figure "200" should read "220".

2. On page 24892:

a. In paragraph 6. in the first column, the word "solultion" in the last line should read "solution".

b. In the table in the second column, the second figure "2.70", under the heading "Sample size, milliliter", should read "2.00".

c. The formula under the heading "*Repeatability*" in the third column should be transferred to appear under the heading "*Reproducibility*", which appeared in the first column on page 24893 and the formula which appeared under the heading "*Reproducibility*" should be transferred to appear under the heading "*Repeatability*". The formulas should read as follows:

Repeatability

0.0003 g P/U.S. gal
(0.08 mg P/litre)
7% of the mean

Reproducibility

0.0005 g P/U.S. gal
(0.13 mg P/litre)
13% of the mean

3. In the second column on page 24893, delete the word "and" which appeared in the fifth line of paragraph 4.11.

APPENDIX B GLOSSARY OF SYMBOLS

This is a glossary of symbols as used in this document. Symbols used and defined in the reference method (appendix A) are not repeated here.

SYMBOL	DEFINITION
Å	Angstrom
cm^3	Cubic centimeter
cm	Centimeter
gal	Gallon
g	Gram
h	Hour
ℓ	liter
mℓ	Milliliter
mm	Millimeter
nm	Nanometer
P	Phosphorus
sp gr	Specific gravity
μ	Micron
μg	Microgram
/	Per
N	Lot size--i.e., the number of determination periods to be treated as a group
n	Sample size for the quality audit (section 3.3)
r	Repeatability of the measurement method at the 95-percent confidence level
$\sigma\{X\}$	Assumed standard deviation of the parameter X (population standard deviation)
s_X	Computed standard deviation of a finite sample of measurements (sample standard deviation)
μ_X	Assumed mean value of the parameter X (population mean)
$\overline{X}$	Computed average of a finite sample of determinations (sample mean)
$\hat{\tau}_X$	Computed bias of the parameter X for a finite sample (sample bias)

APPENDIX B GLOSSARY OF SYMBOLS--CONTINUED

SYMBOL	DEFINITION
R	Reproducibility of the determination method (section 3.0)
R	Range; i.e., the difference in duplicate determinations of a gasoline sample (section 3.2)
d_j	The difference in the audit value and the determined value arrived at by the analyst for the j^{th} audit
$\bar{d}$	Mean difference between known and determined values of reference samples for n audits.
s_d	Computed standard deviation of difference between known and determined values.
P	Percent of determinations outside specified limits L and U (section 3.4)
k	Constant used in sampling variables (section 3.4)
p{Y}	Probability of event Y occurring
σ_r	Repeatability standard deviation
σ_R	Reproducibility standard deviation
t_{n-1}	Statistic used to determine if the sample bias, $\bar{d}$, is significantly different from zero (t-test)
$\frac{\chi^2}{f}$	Statistic used to determine if the sample variance, s^2, is significantly different from the assumed variance, σ^2, of the parent distribution (chi-square test)
L	Lower quality limit used in sampling by variables
U	Upper quality limit used in sampling by variables
CL	Center line of a quality control chart
LCL	Lower control limit of a quality control chart
UCL	Upper control limit of a quality control chart
P_c	Determined phosphorus in a gasoline sample in µg P/l
P_m	Total phosphorus as read from the calibration curve in µg P

APPENDIX C GLOSSARY OF TERMS

The following glossary lists and defines the terms as used in this document

Absorbance	The logarithm to the base 10 of the reciprocal of transmittance.
Accuracy	A measure of the error of a process expressed as a comparison between the measured value and the true value.
Bias	The systematic or nonrandom component of system error.
Chain of custody label	The seal placed on the container which contains the gasoline sample from the test station.
Determination method	A set of procedures for making a determination.
Determination process	The process of making a determination including method, personnel, equipment, and environmental conditions.
Liter	Special name for the cubic decimeter.
Lot	A specified number of objects to be treated as a group.
Population	A very large number of like objects (i.e., measurements, checks, etc.) from which the true mean and standard deviation can be deduced with a high degree of accuracy.
Precision	The degree of variation among measurements on a homogeneous material under controlled conditions and usually expressed as a standard deviation or as a coefficient of variation.
Quality audit	A management tool for independently assessing data quality.
Quality control check	Checks made by the operator on certain items of equipment and procedures to assure data of good quality.

APPENDIX C GLOSSARY OF TERMS (CONTINUED)

Reference sample	Sample submitted to the laboratory for quality control check (concentration unknown to the analyst).
Sample	Objects drawn usually at random from the lot for checking.
Spectral bandwidth	The range of wavelengths between the two points at which the absorbance is one-half the peak absorbance.
Standard sample	Sample prepared by the technician from the stock standard solution to check the phosphorus calibration curve.
Test station	Retailer gasoline station or distributor serving the public.